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PROCEEDINGS OF THE INTERNATIONAL LIME/LIMESTONE WET-SCRUBBING SYMPOSIUM (2nd), HELD AT NEW ORLEANS, LOUISIANA ON NOVEMBER 8-12, 1971. VOLUME 1

National Environmental Research Center

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June 1972

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PROCEEDINGS

SECOND INTERNATIONAL

LIME/LIMESTONE

WET-SCRUBBING SYMPOSIUM

VOLUME I

November 8-12, 1971
Sheraton-Charles Hotel
New Orleans, Louisiana

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ENVIRONMENTAL PROTECTION AGENCY
Office of Administration
Research Triangle Park, North Carolina
June 1972

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Publication Number APTD-1161

PREFACE

The Second International Lime/Limestone Wet Scrubbing Symposium was held November 8-12, 1971, in the Claiborne Room of the Sheraton-Charles Hotel, New Orleans, Louisiana, sponsored by the Environmental Protection Agency, Office of Air Programs, Control Systems Division.

The Symposium, under the chairmanship and vice-chairmanship of Messrs. E.L. Plyler and D.R. Mayfield, began Monday morning with the official welcome and opening remarks by OAP's Sheldon Meyers, followed by an introduction by Mr. Plyler.

The Symposium consisted of nine sessions, divided into five different areas: fundamental research, pilot scale research and development, prototype and full scale tests, panel discussion on scaling, sampling and analytical methods.

Sessions 1 and 2, chaired by Philip S. Lowell, were concerned with fundamental research. Frank T. Princiotta of OAP was the chairman for Sessions 3 and 4 and the first three presentations of Session 5, dealing with pilot scale research and development.

The last two presentations of Session 5 and Sessions 6 and 7 were chaired by H.W. Elder. The 17 papers presented in these sessions were concerned with prototype and full scale tests.

The panel discussion on problems related to scaling in lime/limestone wet scrubbing, chaired by A.V. Slack, consisted of the five papers of Session 8. OAP's J.A. Dorsey chaired Session 9, sampling and analytical methods, which concluded the symposium early Friday afternoon.

All papers presented during the symposium are included in these proceedings except those which were given by notes and for which there exists no written text.

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FUNDAMENTAL RESEARCH

Philip S. Lowell, Chairman

Participants:

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M. Epstein, C.C. Leivo, C.H. Rowland
Delbert M. Ottmers, Jr.
James L. Phillips
D.C. Drehmel
J.M. Potts, A.V. Slack, J.D. Hatfield
L.H. Garcia
J.D. Hatfield and J.M. Potts
J.S. Morris
Linda Z. Condry, Richard B. Muter,
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SUMMARY
FUNDAMENTAL RESEARCH
(PARTS I AND II)

Philip S. Lowell, Chairman

Lime and limestone based processes for control of SO_2 emissions from boiler flue gases are nearing commercialization. The overall process involves removing SO_2 from the flue gas in a scrubber. In auxillary portions of the system the lime or limestone is dissolved. Calcium sulfite and sulfate are precipitated and removed from the system.

The objective of the research part of process development is to provide an understanding of the process. This understanding of lime/limestone wet scrubbing processes will provide the basis for several functions:

- design of laboratory and pilot plant tests,
- provision of a framework within which experimental data may be interpreted,
- provision of the basis for extrapolating from bench and pilot work to full size, i.e., process design data and methods,
- solution of operating problems.

The major subjects of fundamental research involve the chemical reactions, mass transfer steps, equipment characteristics, and the interactions of the above three. In addition to the main thrust of process development there are potential ancillary problems that must be solved. Two of these are solid waste disposal and prevention of ground and stream water pollution.

SIMULATION OF SO_2 ABSORPTION IN A VENTURI SCRUBBER BY ALKALINE SOLUTIONS

CONTRACT NO. EHS-D-71-20

Prepared for:

Lime/Limestone Wet Scrubbing Symposium

New Orleans, Louisiana

8-12, November 1971

By

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1. Introduction

Although venturi scrubbers are widely used for simultaneous removal of gaseous and particulate pollutants, studies of mass transfer and chemical reactions taking place in venturi scrubbers have been few. Operations of venturi scrubbers usually involve gas, liquid, and solid phases with considerable pressure drops in the system.

The work presented here is sponsored by the Office of Air Programs, Environmental Protection Agency, and is an attempt to elucidate the phenomena taking place in the venturi-type absorber both from the mechanical and absorption kinetic points of view. The design and scale-up criteria of the venturi scrubber can thus be developed so that more efficient and economic commerical scrubbers can be built. To meet this goal, mathematical models are developed and the performances of various venturi scrubbers are simulated and then compared with the experimental data available.

It is hoped that the models developed can be used as an aid in the design and scale-up of venturi scrubbers for SO_2 absorption under different operating conditions.

2. Mechanics of Venturi Scrubber Operations

a. Pressure Drop in a Venturi Scrubber

Pressure drops for gas flowing through a venturi scrubber are estimated by knowing the effects of friction along the wall of the equipment and the acceleration of liquid. Frictional loss depends largely upon the geometry of the scrubber and must be determined experimentally.

The effect of acceleration of liquid is, however, predictable theoretically.

Several correlations available in the literature are summarized in Table 1.

Matrozov's correlation [16] and Volgin's correlation [22] were obtained mainly on small size venturi scrubbers. Calvert [2] derived a pressure drop equation by use of Newton's Law to obtain the force · required to change the momentum of liquid at a given rate. This equation and Volgin's correlation do not contain the term responsible for the frictional loss on the wall of the venturi scrubber, which becomes negligibly small at a high liquid rate in comparison with the acceleration loss.

The fourth correlation has been obtained experimentally for Flooded Disk scrubbers using the sodium carbonate solution by Cottrell Environmental Systems, Inc. [6]

b. Mean Diameter of a Liquid Droplet

Various correlations are available in the literature to estimate the mean liquid drop diameter from different types of atomizers under different operating conditions. These correlations are applicable within a certain range of operating conditions and properties of fluids; such as volume ratio of gas to liquid, relative velocity of gas to liquid, type of nozzle, surface tension of liquid, etc. In using one of these correlations to estimate the droplet diameter, it is important to select a proper correlation which takes these factors into consideration.

Applicabilities of various correlations in terms of the range of mass ratio of gas to liquid, the relative velocity of gas to

Table I. Correlation for Pressure Drop

Investigator (Reference)		Equation
Matrozov	(16)	$\Delta P_1 = \Delta P_d + 18 w^{1.08} m^{0.63}$
Volgin, et.al.	(23)	$\Delta P_2 = 2.22 \times 10^{-2} w^2 q^{0.26} \ell^{0.143}$
Calvert	(2)	$\Delta P_3 = 5 \times 10^{-5} (v_g)^2 R$
Gleason & Mckenna	(6)	$\Delta P_4 = 4.86 \times 10^{-6} v_g^{\,2} (L + 73.8)$

liquid, and the viscosity of liquid are shown in Table II. Among these correlations, probably the best known and the most widely used is that of Nukiyama and Tanasawa [18]. Analysis of this correlation shows that its applicability is limited to the range of high relative velocities and large mass ratio of gas to liquid.

Kim and Marshall [12] recently developed a correlation which covers a wide range of important variables. Their correlation has a form similar to the Nukiyama-Tanasawa equation, but predicts smaller droplet sizes under similar operating conditions. The Nukiyama-Tanasawa equation was based on data obtained by physical sampling technique which probably introduced some errors due to the evaporation and target effect to the sample collecting device. Kim and Marshall [12] also reported that a modified form of their correlation can be used to correlate Wetzel's drop-size data [24] for venturi atomization.

c. Equation of Motion of a Liquid Drop

Assuming that there is no change in the drop diameter, and that every droplet has the same diameter, velocities of gas and liquid can be calculated as follows.

The average gas velocity at any point in a venturi scrubber is calculated by the following relation:

$$v_g = \frac{G_O}{\epsilon S}$$

The velocity of a droplet can be calculated by

$$v_L = \frac{L_O}{(1-\epsilon)S}$$

Table II Empirical Equations for Droplet Diameter and their Applicable Ranges

Investigator [Reference]	Equation	Applicable Range v_{ro}[ft/sec]	(M_g/M_L)[-]	μ_L[c.p.]
Nukiyama, S. and Y. Tanasawa (1939) [18]	$D_{32} = 585\frac{\sqrt{\sigma}}{v_{ro}\sqrt{\rho_L}} + 597\left(\frac{\mu_L}{\sqrt{\sigma\rho_L}}\right)^{0.45} \cdot \left(1000\frac{L_o}{G_o}\right)^{1.5}$	300 to sonic velocity	1.8 to 15	1 to 46
Mugele, R.A. (1960) [17]	$\frac{D_{32}}{D_n} = A\left(\frac{D_n\rho_L v_{ro}}{\mu_L}\right)^B \cdot \left(\frac{\mu_L v_{ro}}{\sigma}\right)^C$	300 to sonic velocity	1.8 to 15	--
Gretzinger, J. and W.R. Marshall (1961) [7]	$D_m = 2600\left[\left(\frac{M_L}{M_g}\right)\cdot\left(\frac{D_n v_{go}\rho_g}{\mu_g}\right)\right]^{0.4}$	300 to sonic velocity	1 to 15	1 to 30
Wigg, L.D. (1964) [25]	$D_m = 2X10^4\left(\frac{\mu_L}{\rho_L}\right)^{1/2} \cdot M_L^{0.1}\left(1+\frac{M_L}{M_g}\right)^{1/2} \cdot D_n^{0.1}\ \sigma^{0.2}\rho_g^{-0.3}v_{ro}^{-1}$	270 to 1150	0.5 to 20.2	3.2 to 45
Kim, K.[illegible]. and W.R. Marshall (1971) [12]	$D_m = 249\frac{\sigma^{0.41}\mu_L^{0.32}}{(v_{ro}^2\rho_g)^{0.57}S^{0.36}\rho_L^{0.16}}$ $+ 1260\left(\frac{\mu_L^2}{\rho_L\sigma}\right)^{0.71} \cdot \frac{1}{v_{ro}^{0.54}}\left(\frac{M_g}{M_L}\right)^m$ $m = -1 \quad \text{for } M_g/M_L < 3$ $m = -0.5 \text{ for } M_g/M_L > 3$	250 to sonic velocity	0.06 to 40	1 to 50

Equation of motion of a liquid drop can be written from the momentum balance of a drop within the flowing gas as follows [10]:

$$\rho_L\left(\frac{\pi D_p^3}{6}\right)\frac{dv_L}{dt} = \rho_L\left(\frac{\pi D_p^3}{6}\right)g - \rho_g\left(\frac{\pi D_p^3}{6}\right)g + C\left(\frac{\pi D_p^2}{4}\right)\frac{\rho g}{2}(v_g-v_L)|v_g-v_L| \tag{1}$$

If the motion of the droplet is in the vertical direction, the second term can be neglected in comparison to other terms. Since, $\frac{dZ}{dt} = v_L$, the above equation can be written as

$$\frac{dv_L}{dZ} = \frac{g}{v_L} + \frac{3}{4} \cdot \frac{C}{D_p} \cdot \frac{\rho_g}{\rho_L} \cdot \frac{(v_g-v_L)|v_g-v_L|}{v_L} \tag{2}$$

If the motion is in the horizontal direction, the term due to gravity can be neglected and simplified to

$$\frac{dv_L}{dZ} = \frac{3}{4} \cdot \frac{C}{D_p} \cdot \frac{\rho_g}{\rho_L} \cdot \frac{(v_g-v_L)|v_g-v_L|}{v_L} \tag{3}$$

3. Gas Absorption Rate in a Venturi Scrubber

Although a number of studies on mass transfer in venturi scrubbers are available, many of these studies were limited to small laboratory size apparatus and therefore application of these data to industrial size scrubbers must be made with extreme caution.

Mass transfer in a venturi scrubber can be affected by many complex factors such as non-spherical effect of the droplet, coalescence and breaking up of the drops, absorption by the liquid on the equipment wall, etc. A number of simplifying assumptions are therefore made in the analysis of SO_2 absorptionby an alkali solution in a venturi scrubber.

These are:

- -- No coalescence or breaking up of the droplets occurs after atomization. Droplets keep the same mean diameter as that created at the nozzle point.
- -- Liquid droplets are all spherical.
- -- The variation in droplet diameter due to evaporation may be neglected.
- -- Heat of reaction is negligibly small.

a. Overall Rate of SO_2 Absorption into Droplets of Alkaline Solutions.

The kinetic theory of simultaneous diffusion and chemical reaction in the liquid phase has been developed by Hatta [8], Davis, et. al [3], and others based on the two-film theory for physical absorption originally proposed by Lewis and Whitman [14].

The experimental results obtained by Linn, et. al. [15] and Hikita, et. al. [9] indicate that the absorption of SO_2 by water may be considered as physical absorption. The agreement of data for SO_2-alkaline systems obtained by Hikita, et. al. [9] and Onda, et. al. [19] with that calculated by the physical penetration theory suggest that the absorption rates are predictable in the same way as that tor the SO_2-H_2O system. The rate of SO_2 absorption may be given by

$$N_A = \frac{C_e - C_L}{(1/k_L) + (H/k_g)} = \frac{C_e - C_L}{1/K_L} \qquad (4)$$

b. Mass Transfer and Heat Transfer Coefficients of Liquid Droplet

Gas-phase mass transfer to or from a single sphere placed in a moving fluid has been studied by many investigators [5, 13, 21]. One of the correlations having the same form as the Ranz-Marshall equation obtained by Steinberger and Treybal [22] can be used to calculate the gas-phase mass transfer coefficient for each drop in a venturi scrubber,

$$N_{Sh} = N_{Sho} + 0.347(N_{Re} \cdot N_{Sc}^{1/2})^{0.62} \tag{5}$$

where N_{Sho} can be calculated by

$$N_{Sho} = 2 + 0.569(N_{Gr}\ N_{Sc})^{0.25}$$

$$\text{for } (N_{Gr}\ N_{Sc}) < 10^8$$

$$N_{Sho} = 2 + 0.0254(N_{Gr}\ N_{Sc})^{1/3} N_{Sc}^{0.244}$$

$$\text{for } (N_{Gr}\ N_{Sc}) > 10^8$$

For all practical purpose, $N_{Sho} \cong 2$, and the above equation becomes

$$N_{Sh} = 2 + 0.347(N_{Re}\ N_{Sc}^{1/2})^{0.62} \tag{6}$$

The ranges of applicability for this correlation are

$$1 < N_{Re} < 30{,}000$$

$$0.6 < N_{Sc} < 3{,}000$$

The mass transfer coefficient, k_c, is related to k_g by

$$k_c = RTk_g$$

A similar type of correlation as equation (6) is used for the mass transfer coefficient of water vapor from the surface of liquid drop to gas phase.

In contrast to the extensive studies made on mass transfer around a sphere, no correlation for the mass transfer coefficient inside the sphere is available. Although liquid circulation or turbulence in the droplet may be possible, it is assumed that the drop is a rigid sphere and that there is no movement of the liquid within the droplet. For an unsteady state gas absorption of gas into a drop, the mass transfer coefficient in the liquid phase can be obtained as follows:

$$\frac{\partial C_L}{\partial t} = \frac{D}{r^2} \cdot \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_L}{\partial r}\right) \qquad (7)$$

I.C.: $t = 0;\ 0 < r < r_o;\ C_L = 0$

B.C.: $t > 0;\ r = r_o;\ C_L = C_L^*$

This equation can be solved analytically to obtain the rate of absorption at time t as:

$$N_A = \frac{2DC_L^*}{r_o} \sum_{m=1}^{\infty} \exp\left(-\frac{Dm^2\pi^2 t}{r_o^2}\right) \qquad (8)$$

The mass transfer coefficient k_L may be defined as:

$$k_L = \frac{2D}{r_o} \sum_{m=1}^{\infty} \exp\left(-\frac{Dm^2\pi^2 t}{r_o^2}\right) \qquad (9)$$

The heat transfer coefficient in the gas-phase needed to calculate the temperature profile is estimated from the following correlation [21].

$$N_{Nu} = 2 + 0.6N_{Re}^{1/2} \cdot N_{Pr}^{1/3} \qquad (10)$$

As the heat transfer in the liquid-phase is much larger than that in the gas-phase, it is assumed that there is no temperature gradient in the liquid droplet.

c. Equilibrium Data and Absorption Rate Data

Equilibrium curves of the SO_2-H_2O system, the 0.01M-NaOH-SO_2 system, and the 0.03M-NaOH-SO_2 system at 77°F are shown in Figure I. The curves for the NaOH-SO_2 system are obtained from the computer program provided by the Radian Corporation [20].

Experimental data obtained from absorption of SO_2 into alkaline solutions by liquid-jet type [9], and stop-cock type [19] absorbers have been correlated in the present study based on the penetration theory as shown in Figure 2. The fact that the rate of SO_2 absorption in NaOH solution can be represented by a physical absorption mechanism, and since the contact time for the liquid-jet absorber is almost the same as that in a venturi scrubber, equation (9) developed for SO_2 absorption in a spherical droplet seems applicable for SO_2 absorption in a venturi scrubber.

4. Development of Performance Equations for a Venturi Scrubber

From the material and heat balances across a small increment of a venturi scrubber, the following equations can be set up.

$$L_m dx = L_m \cdot \frac{dC_L}{\rho_M} = adV \cdot N_A \tag{11}$$

$$G_m dy_m = k_{gw} a(y_w^* - y_w) dZ = -dL_m \tag{12}$$

$$h_g a(t_g - t_L) dZ = L_m C_{pL} dt_L + \beta k_{gw} a(y_w^* - y_w) dZ \tag{13}$$

$$G_m C_{pg} dt_g = h_g a(t_L - t_g) dZ \tag{14}$$

And

$$dV = SdZ$$

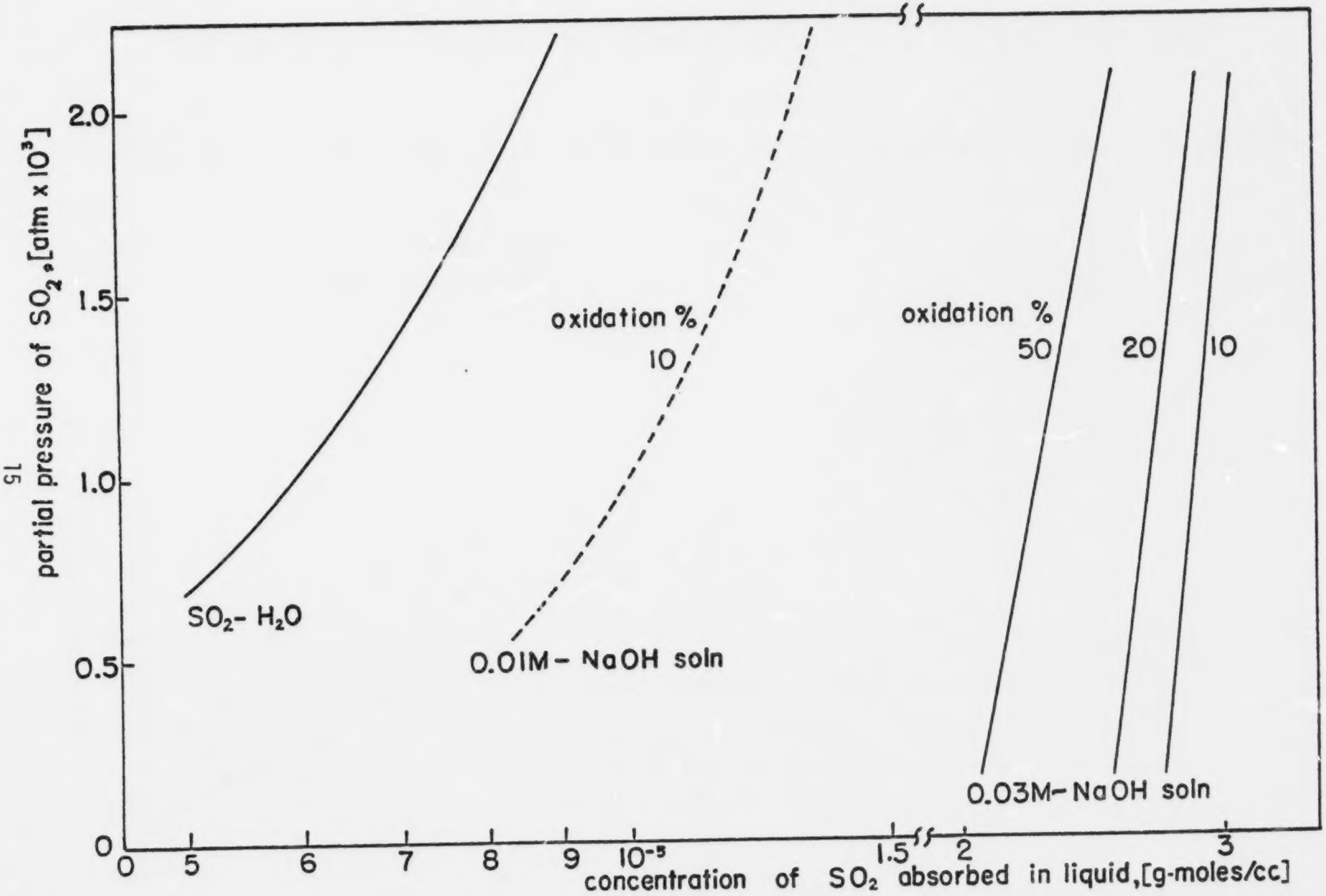


Figure 1. Equilibrium SO_2 Partial Pressure over Various Solutions (77°F)

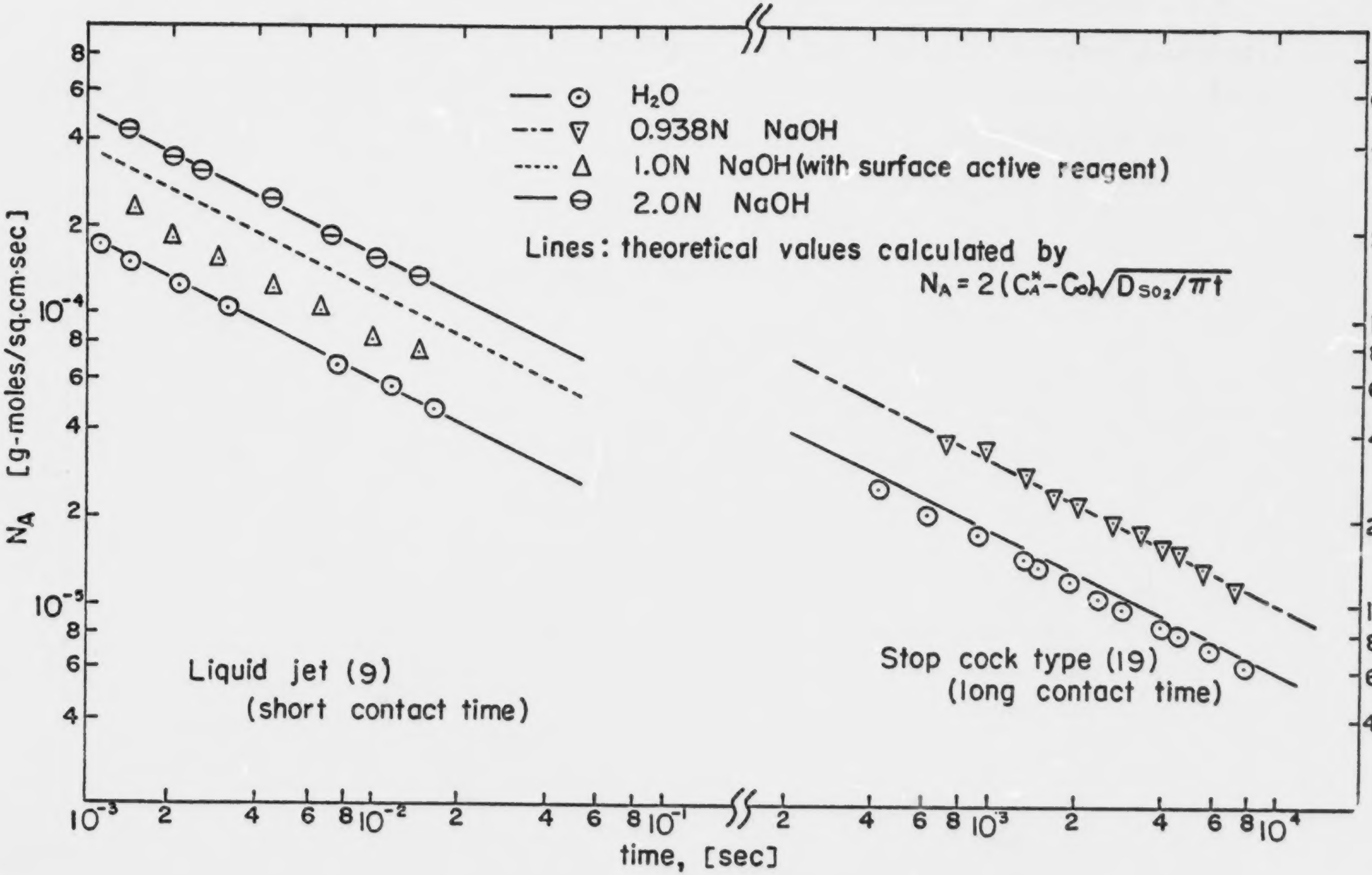


Figure 2. Comparison of Experimental Data on Rate of SO_2 Absorption with Theoretical Values

$$a = \frac{6(1-\varepsilon)}{D_p}$$

Figure 3 illustrates the differential volume used for the material and heat balances and the concentration and temperature profile across the liquid-gas interface.

The water vapor pressure at the interface, $p_w^* = Py_w^*$, can be estimated from Antoine's correlation [1].

$$\log p_w^* = A - \frac{B}{t_L+219} \tag{15}$$

Where

$A = 7.7423$ and $B = 1554.16$ for $t_L = 35 \sim 55$ [°C]

$A = 7.8097$ and $B = 1572.53$ for $t_L = 55 \sim 85$ [°C]

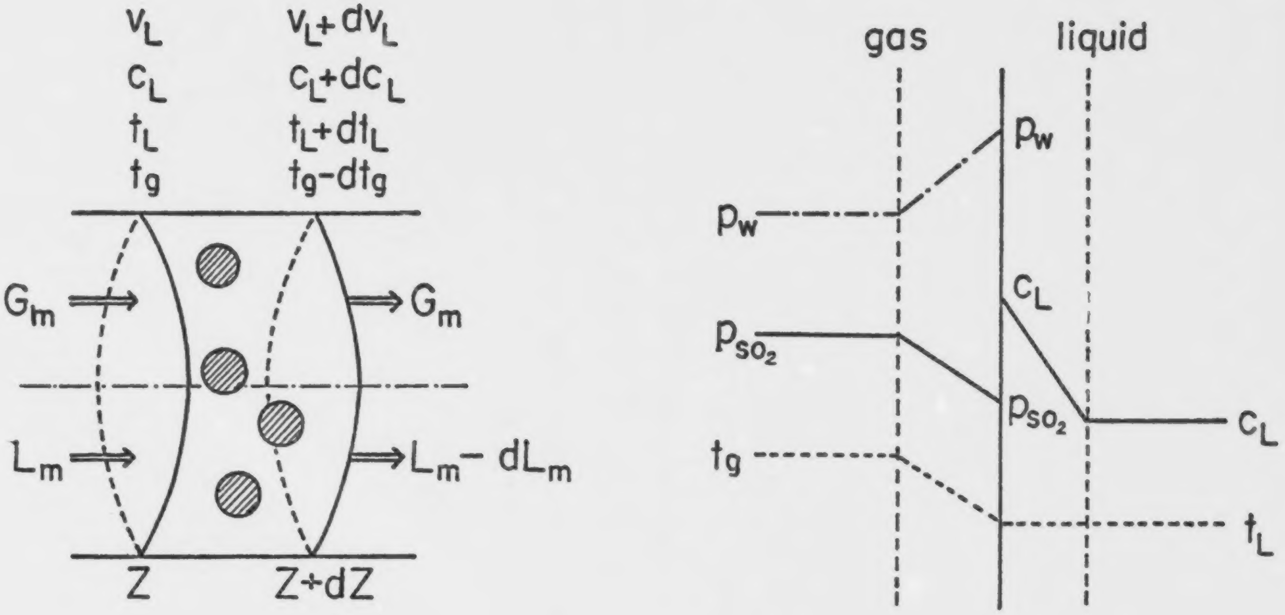
From the heat and mass balance equations and the flow equations developed, the following differential equations relating liquid velocity, SO_2 concentration in liquid, H_2O mole fraction in gas phase, temperatures of gas and liquid, molar liquid rate, and contact time with respect to Z are obtained as follows:

$$\frac{dv_L}{dZ} = \frac{g}{v_L} + \frac{3}{4} \cdot \frac{C}{D_p} \cdot \frac{\rho_g}{\rho_L} \frac{(v_g-v_L)|v_g-v_L|}{v_L} \tag{16}$$

$$\frac{dC_L}{dZ} = \frac{K_L a \rho_M}{L_m/S} \cdot (C_e - C_L) \tag{17}$$

$$\frac{dy_w}{dZ} = \frac{k_{gw} a}{G_m} \cdot (y_w^* - y_w) \tag{18}$$

$$\frac{dt_L}{dZ} = \frac{1}{L_m C_{pL}} [h_g a(t_g - t_L) + \beta k_{gw} a(y_w^* - y_w)] \tag{19}$$



(a)

(b)

Figure 3 (a) Schematic Diagram of a Differential Element in a Venturi Scrubber
(b) Concentration and Temperature Profiles at Interface

$$\frac{dt_g}{dZ} = \frac{h_g a}{G_m C_{pg}} (t_L - t_g) \tag{20}$$

$$\frac{dL_m}{dZ} = - k_{gw} a (y_w^* - y_w) \tag{21}$$

$$\frac{dt}{dZ} = \frac{1}{v_L} \tag{22}$$

These equations can be numerically solved using the following initial conditions:

$v_L = v_{Lo}$

$C_L = C_{Lo}$

$y_w = y_{wo}$

$t_L = t_{Lo}$

$t_g = t_{go}$

$L_m = L_{mo}$

$t = 0$

5. Simulation of Performances of Various Venturi Scrubbers

a. O.A.P. Experiments

A series of experiments of SO_2 absorption with water and NaOH-solution have been performed by the Office of Air Programs, Environmental Protection Agency using a venturi scrubber shown in Figure . The simulations of the experiments have been conducted using the data provided (Appendix).

The results of calculation on the pressure drop, velocity profiles of gas and liquid, and concentration and temperature profiles for some typical runs are shown in Figures 5, 6, 7, and 8.

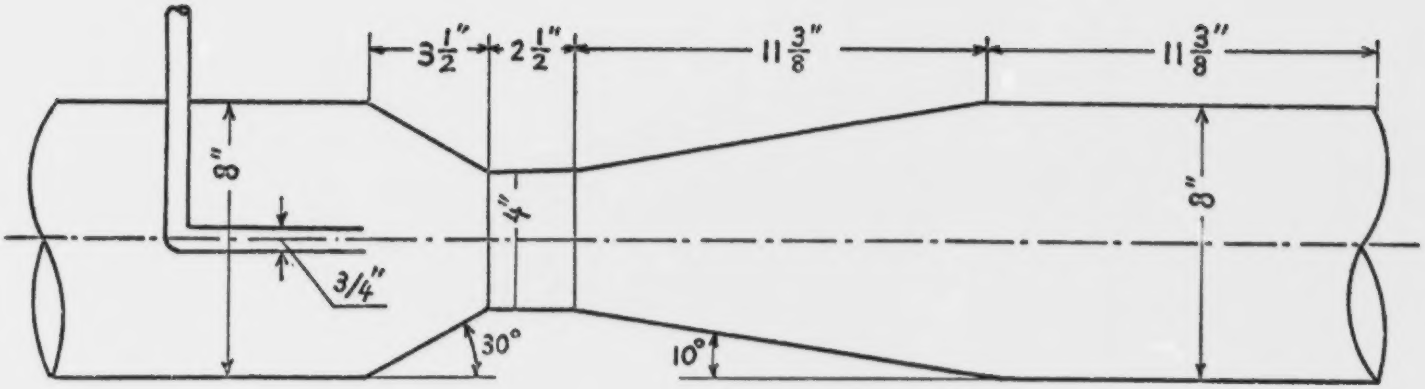


Figure 4. Dimensions of OAP Venturi Scrubber

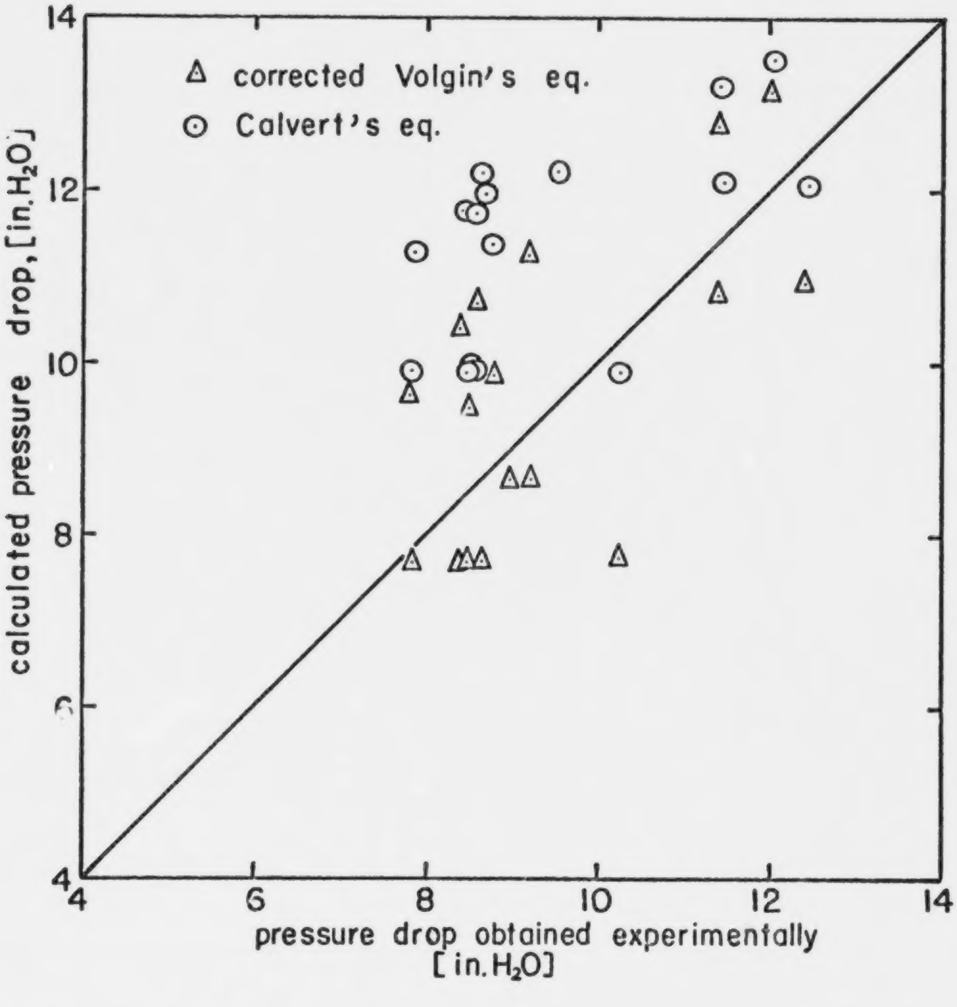


Figure 5 Comparison of Calculated Pressure Drop with Experimental Data (O.A.P. Venturi Scrubber)

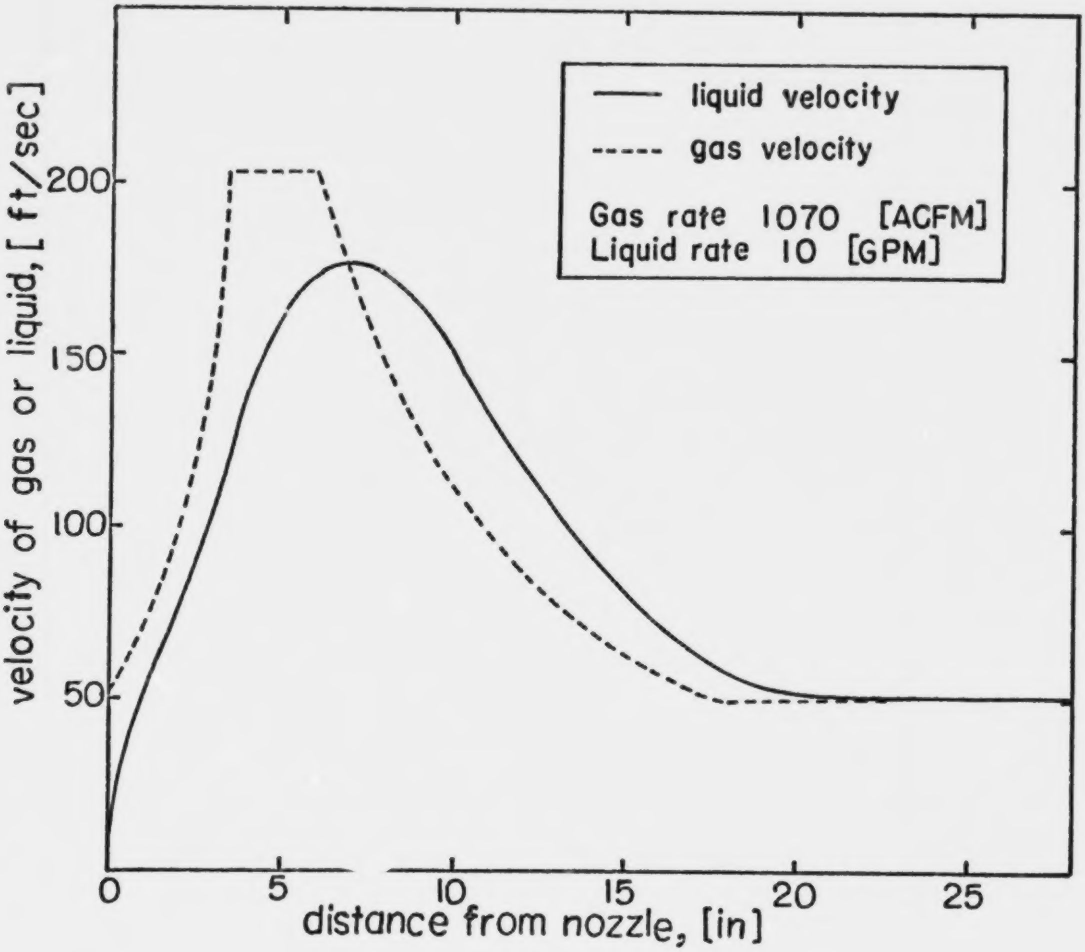


Figure 6. Velocity Profiles of Gas and Liquid along Axial Direction (Run 6) (OAP Exp.)

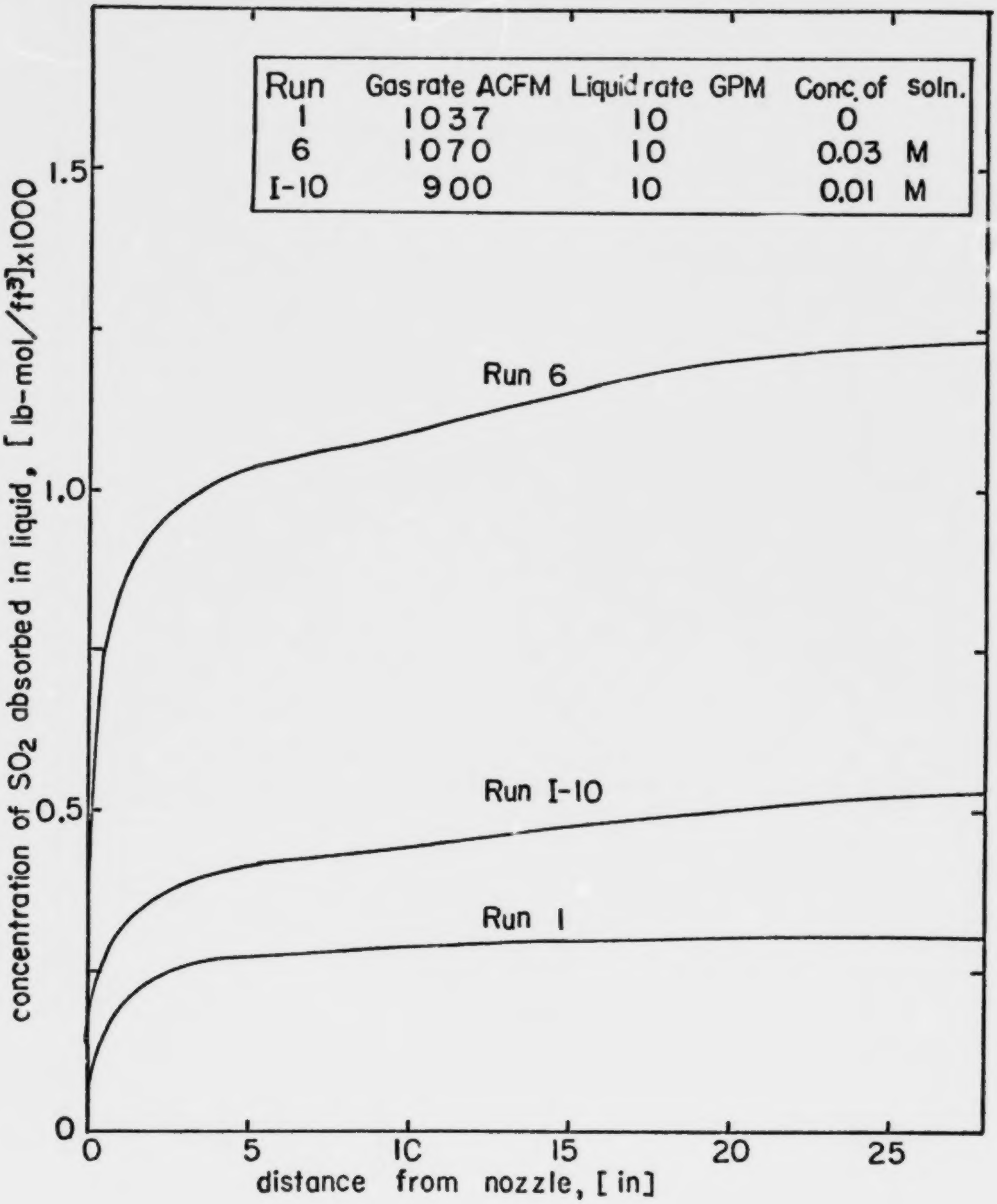


Figure 7 Concentration Profiles of SO_2 Absorbed in Liquid (OAP Exp.)

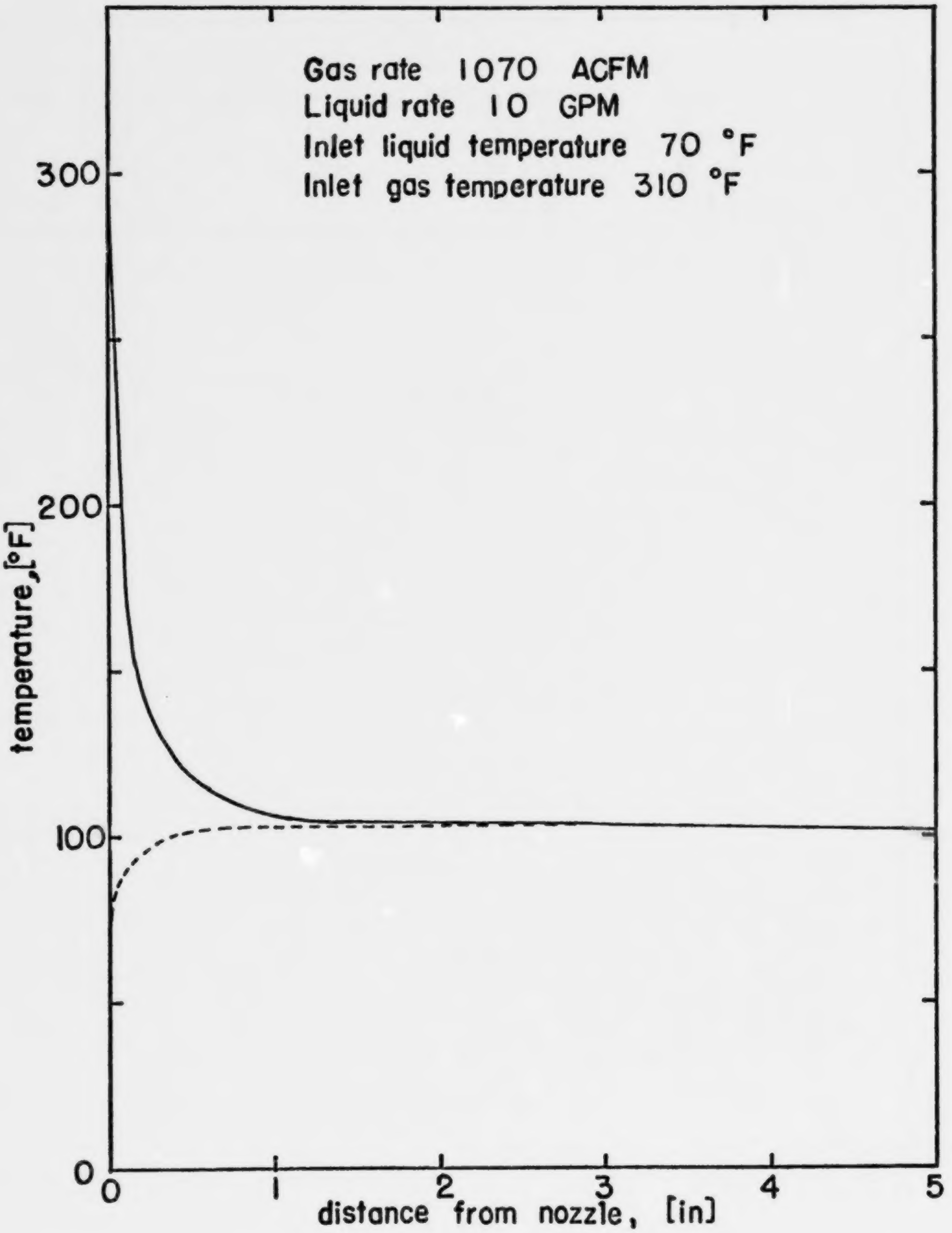


Figure 8 Temperature Profiles of Gas and Liquid (Run 6) (OAP Exp.)

The correlation equation for pressure drops given by Matrożov has two terms, one for frictional loss and the other for acceleration loss. Since the agreement of this correlation with experimental data is rather poor and no trend with respect to the operating condition can be found, his correlation is not included in the figure. The Calvert equation always gives higher values than experimental data even though it does not contain friction loss term. On the other hand, Volgin's correlation takes into account the frictional loss along the throat, but his correlation gives lower values than the experimental data.

For the venturi scrubber used by O.A.P., the pressure drop can be estimated by corrected Volgin equation shown below.

$$\Delta P_2 = 3.5 \times 10^{-2} w^2 q^{0.26} l^{0.143}$$

The liquid concentration profiles presented in Figure 7 show that equilibrium is almost reached within a few inches from the nozzle. Also the temperature profiles in Figure 8 indicate that both gas and liquid attain the same temperature rather quickly. Therefore, the operation can be considered isothermal except for a short section near the nozzle. As can be noticed from the concentration profiles of the liquid shown in Figure 7, the mass transfer rate near the nozzle is so fast that the temperature effect can not be neglected.

The results of simulation of the O.A.P. venturi scrubber experiment are shown in Figure 9 for three types of scrubber liquors, indicating satisfactory agreement.

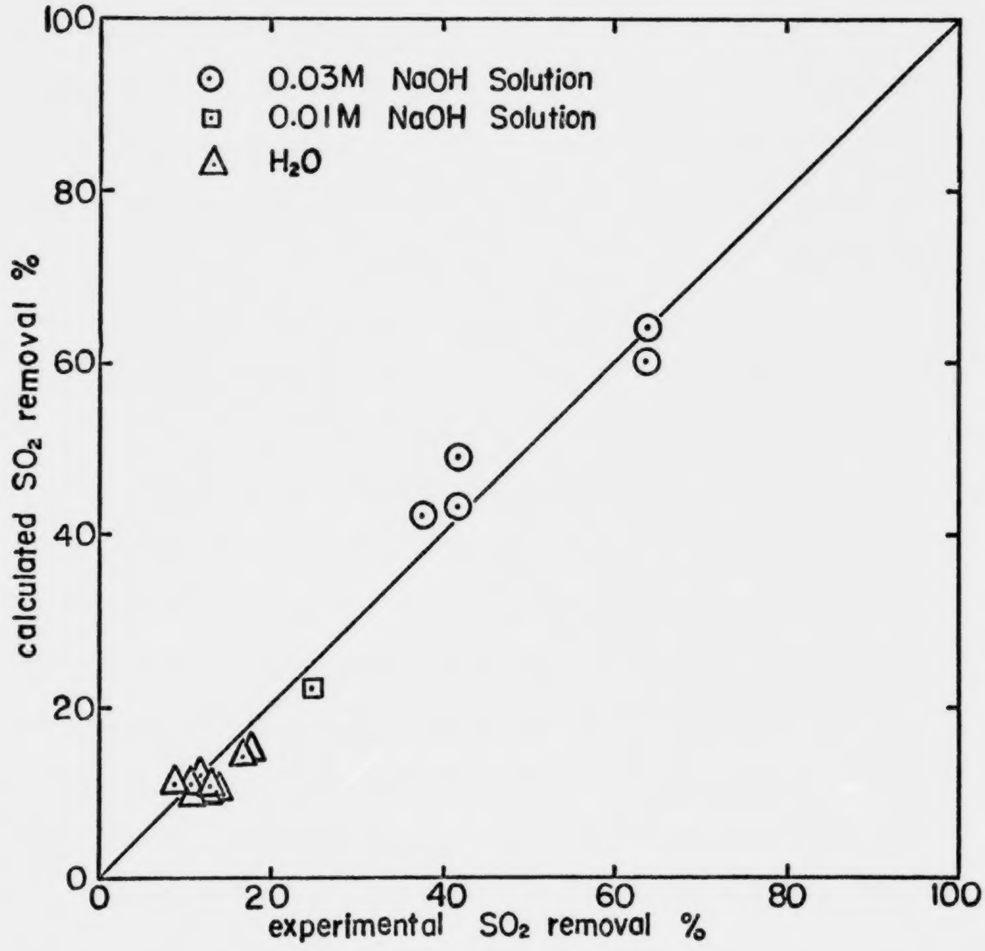


Figure 9 Comparison of Calculated SO_2 Removal % with OAP Experimental Data

b. Experiments of Johnstone, et. al. [11]

Johnstone, et. al., reported a venturi scrubber study in which SO_2 was absorbed in 0.6N-NaOH solutions. The dimensions of their equipment are shown in Figure 10 . The results of simulations of their experiments are compared with the actual experimental data in Figures 11 and 12 . The absorption rate profiles are plotted as a function of distance from the nozzle, and also as a function of liquid flow rate through the venturi scrubber.

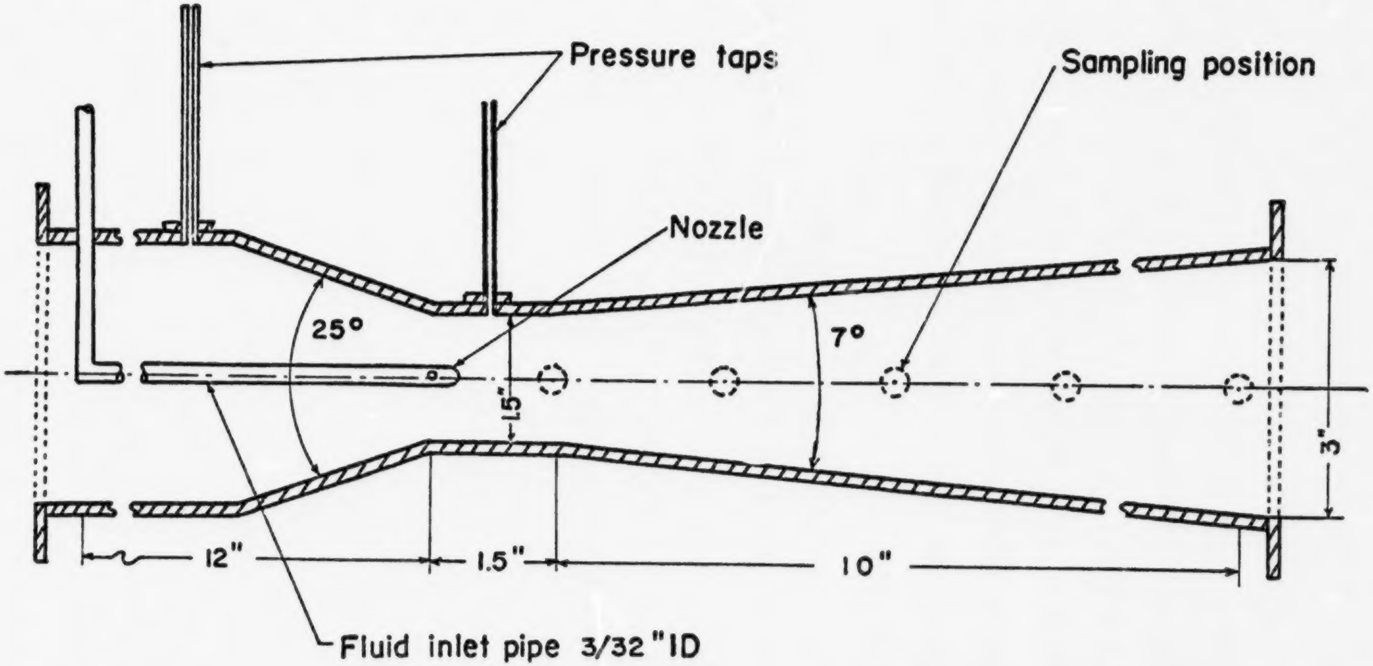
c. Cottrell Environmental Systems' Experiments

The experimental data obtained by Cottrell Environmental Systems, Inc. for the SO_2-lime solution system by Flooded Disk Scrubber are compared with the results obtained from simulation of SO_2 absorption. The dimensions of the equipment and the flow diagram are shown in Figures 13, 14, and 15.

The results of the simulation are given in Figures 16 , 17, and 18.

The pressure drop in the Flooded Disk Scrubber can be predicted rather well by the Calvert equation as shown in Figure 16 . This correlation seems to apply for Flooded Disk-type or short throat type scrubbers since the friction loss has been neglected in the equation. The liquid concentration profile, not shown in this paper, has a similar shape as those obtained for the O.A.P. venturi scrubber.

The results of simulations based on 13 runs from FDS data are shown in Figure 18 .



Gas rate	500 ft/sec at throat
Liquid rate	0.03~0.242 GPM
SO_2 inlet conc.	0.00152 atm
Nozzle	4 holes of 0.046"dia.

Figure 10 Dimensions of Venturi Scrubber used by Johnstone et al.

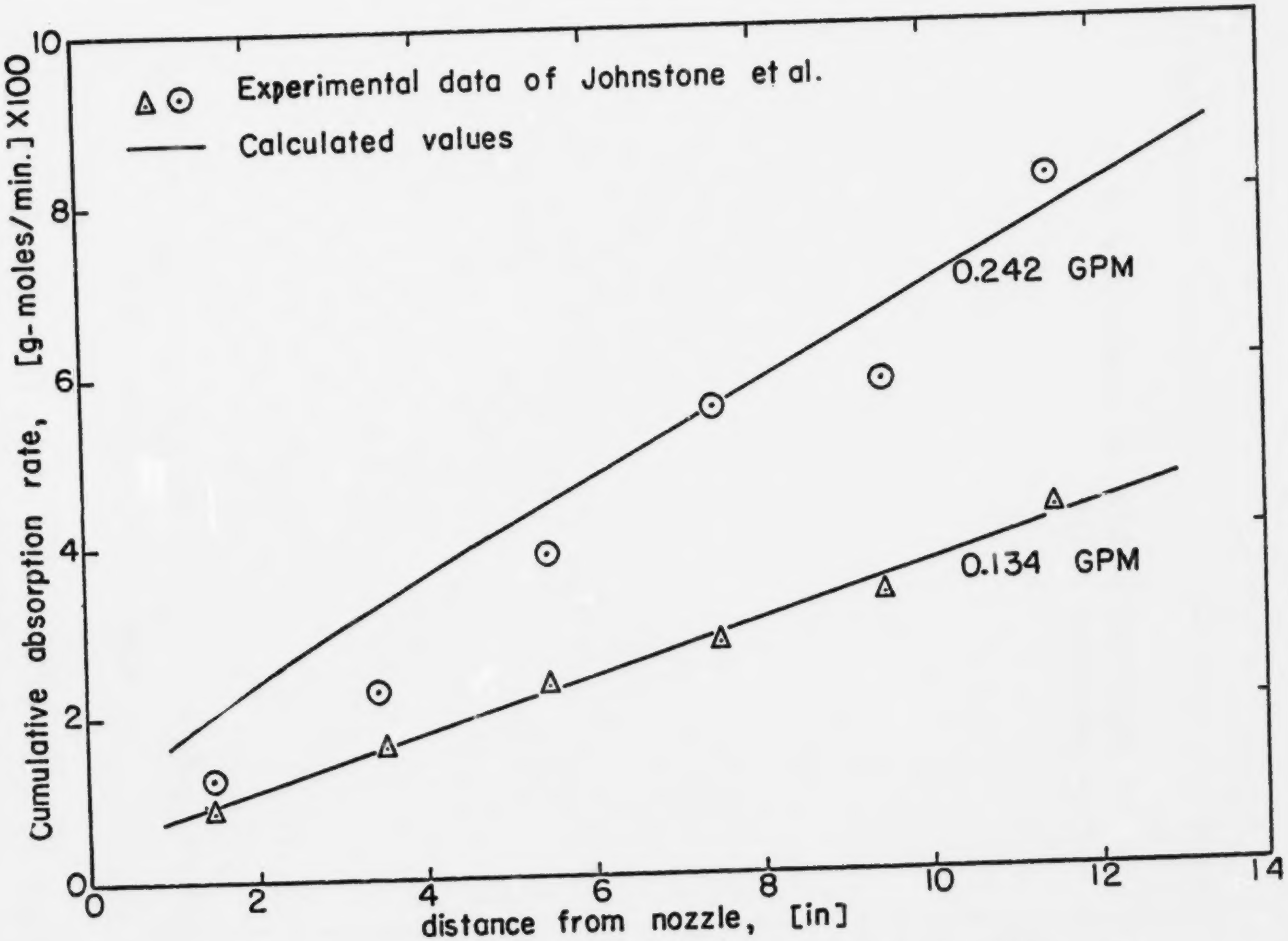


Figure 11. Profiles of Cumulative Absorption Rate in Venturi Scrubber (Experiment of Johnstone et al.)

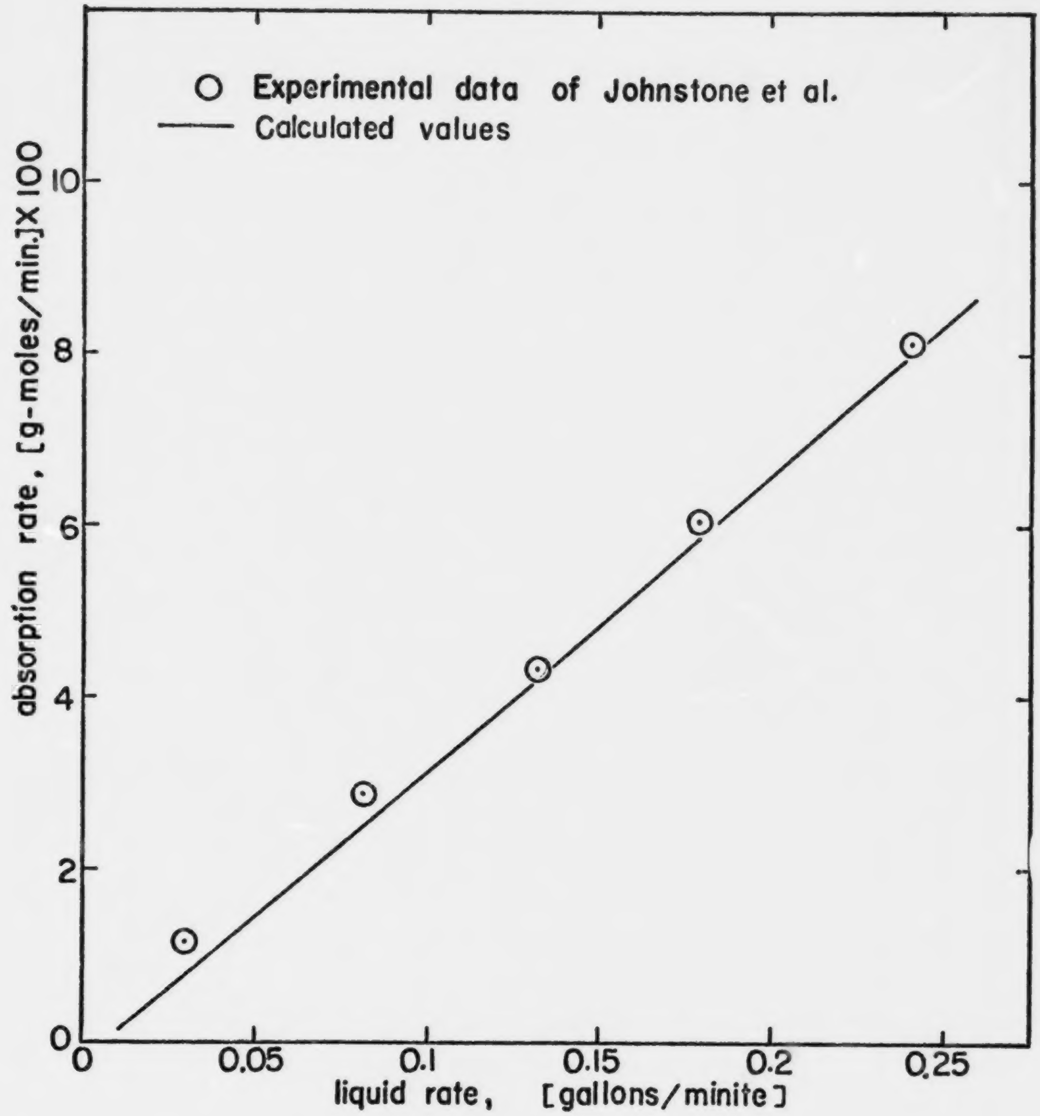


Figure 12 Comparison of SO_2 Removal Rate in the Venturi Scrubber Calculated with Experimental Data Obtained by Johnstone et al

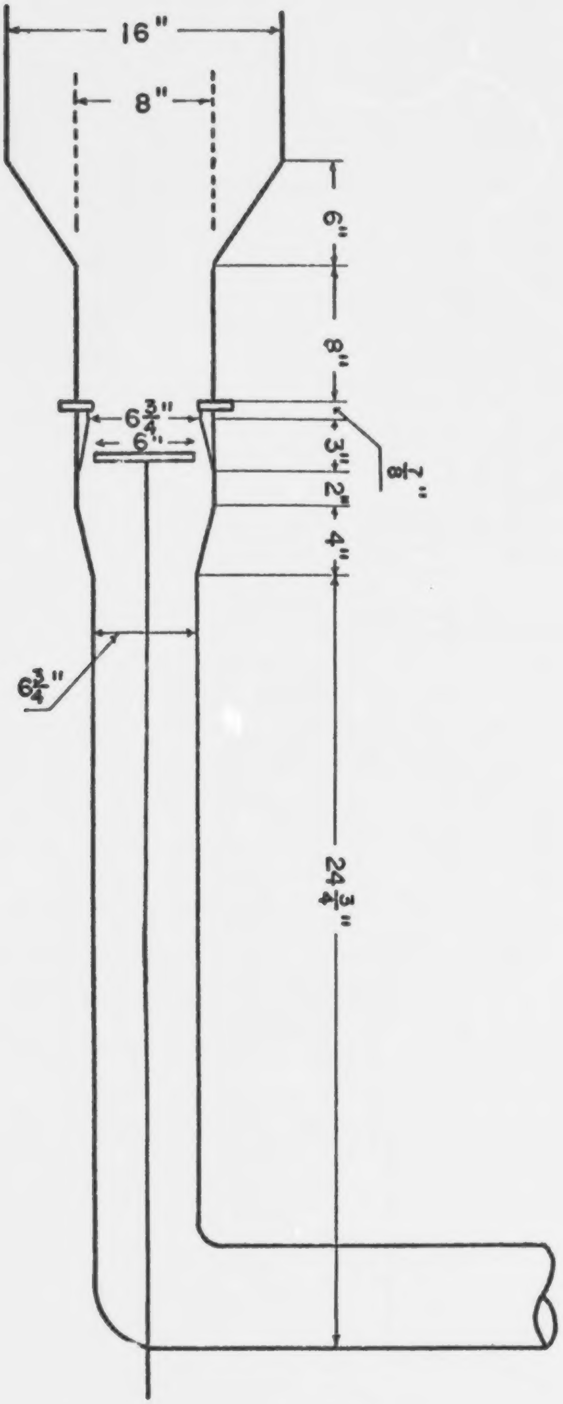


Figure 13. Dimensions of Cottrell's Flooded Disk Scrubber

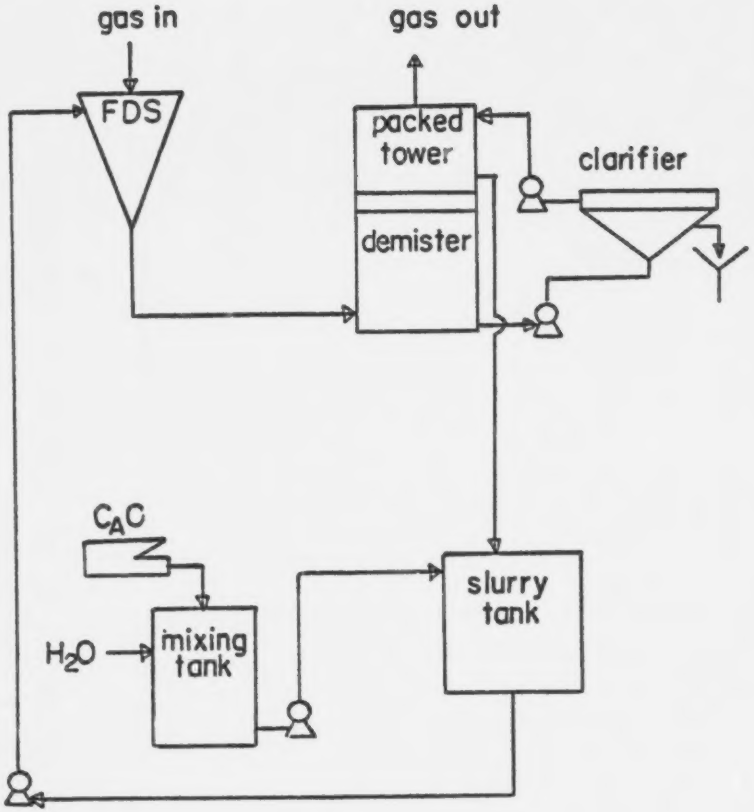


Figure 14 Two Stage Lime Scrubber Wet Slurry (FDS : TASK TT5)

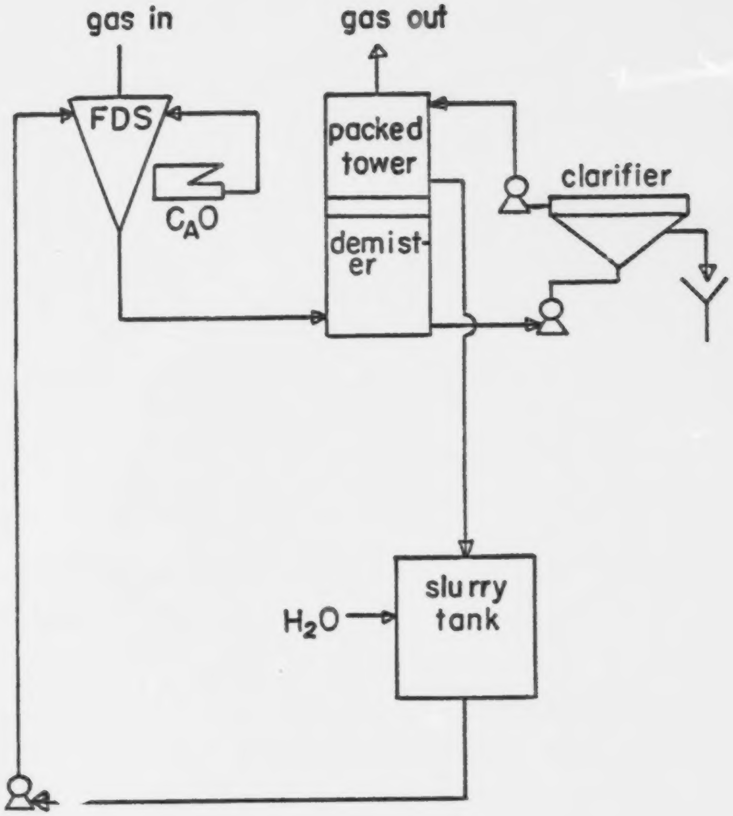


Figure 15. Dry Lime Injection to FDS (FDS : TASK TT6A)

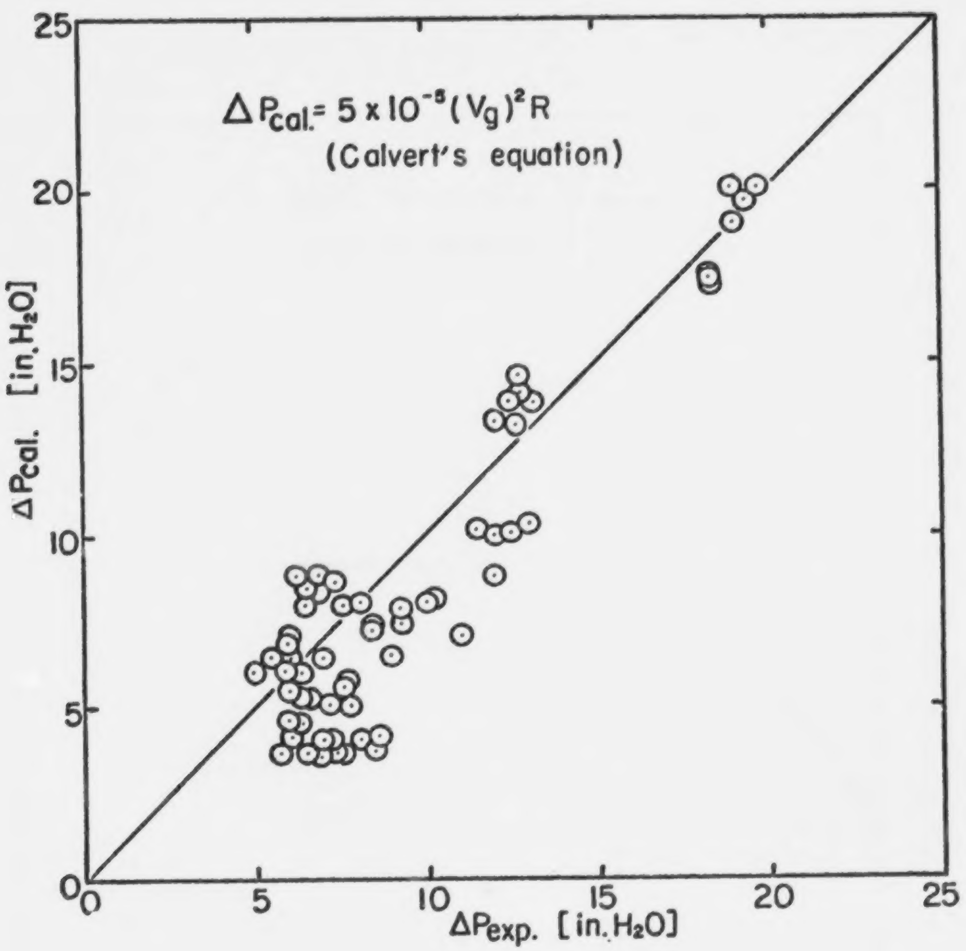


Figure 16. Comparison of Calculated Pressure Drop in FDS with Experimental Data (86 data)

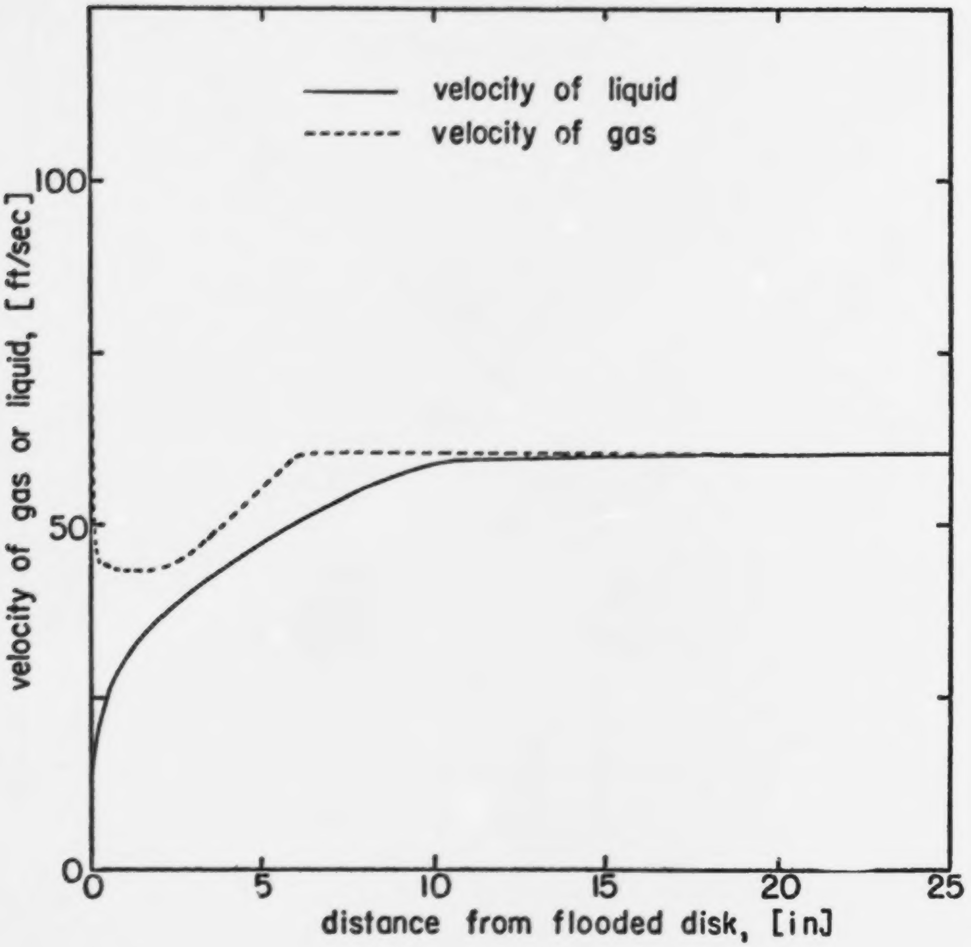


Figure 17. Velocity Profiles of Gas and Liquid in FDS (Task-TT5-2)

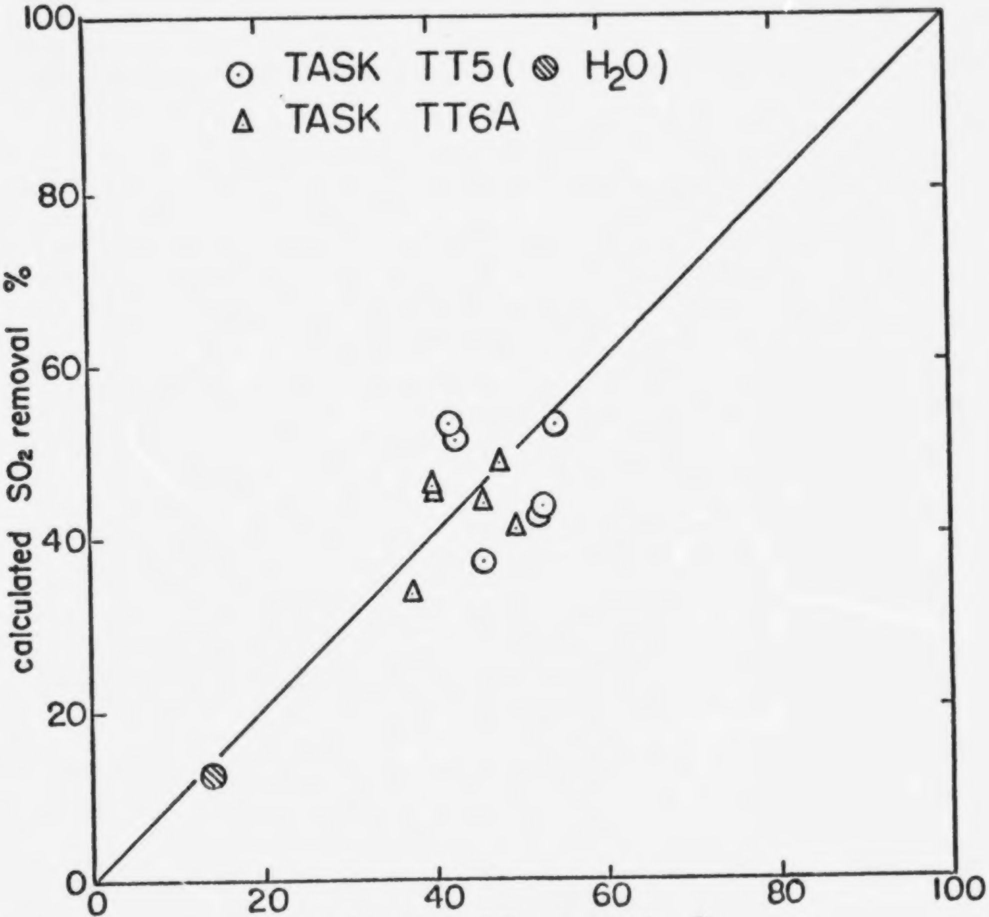


Figure 18 Comparison of Calculated Values of SO_2 Removal % with Those Obtained Experimentally (Cottrell FDS)

6. Conclusion

A mathematical model has been developed to elucidate the mechanism of SO_2 absorption into alkaline solutions and to provide a guide to the scale-up in design of venturi scrubbers. In spite of the assumptions made in the analysis, the results of the simulations show good agreement with the experimental data.

From the results obtained, the following conclusions can be drawn:

-- A significantly large amount of mass and heat transfers take place in a section near the nozzle. This is primarily due to the small transfer resistances, large driving forces, and relatively long residence time of the liquid droplets.

-- The operations of the venturi scrubber can be considered as isothermal except the section within a few inches from the nozzle. High efficiency of the heat transfer is observed in this type of equipment.

-- Near equilibrium concentrations of SO_2 in the liquid were observed at the end of the scrubber in the case of SO_2-H_2O system.

-- Selection of a proper correlation for the mean diameter of a liquid droplet is important in the prediction of the venturi scrubber performance.

Refinement along the following lines will improve the validity of the model developed:

-- The effect of the presence of the solid phase on absorption rate should be examined.

-- The effect of oxidation of sulfite in the liquid phase on absorption and equilibrium must be investigated in more detail.

-- The equilibrium data should be obtained for the systems of SO_2-NaOH solution and SO_2-lime solution to confirm the values estimated by the computer model of Radian cooperation.

-- The formation of the scale, particularly around the nozzle wall, during operation which affects drop and the diameter of the droplet is one of the causes for the deviation of the simulation result from the experiments. Studies to elucidate the cause of scale formation and to develop means of reducing scale are in need.

Notation

a	contact area of gas and liquid per volume, [1/ft]
C	drag coefficient for a particle, [-]
C_e	concentration of SO_2 in liquid phase in equilibrium with partial pressure of SO_2 in bulk phase of gas, [lb-mol/ft^3]
C_L	concentration of SO_2 in liquid phase, [lb-mol/ft^3]
C_L^*	surface concentration of SO_2 in equilibrium with partial pressure of SO_2 at interface, [lb-mol/ft^3]
C_{pg}	specific heat of gas, [Btu/lb-mol. ^oF]
D	diffusivity of SO_2 in liquid phase, [ft^2/sec]
D_m	mass median diameter of a droplet, [micron]
D_n	diameter of a nozzle, [cm]
D_p	diameter of a liquid drop, [ft]
dV	incremental volume of venturi, [ft^3]
D_{32}	surface-volume mean diameter of a droplet, [micron]
g	gravitational acceleration, [ft/sec^2]
G_m	molar gas flow rate, [lb-mol/sec]
G_o	volumetric gas flow rate, [ft^3/sec]
H	Henry's law constant, [lb-mol/ft^3·atm]
h_g	heat transfer coefficient in gas-phase, [Btu/ft^2·sec·^oF]
k	thermal conductivity, [Btu/ft·sec·^oF]
k_c	mass transfer coefficient in gas-phase, [ft/sec]
k_g	mass transfer coefficient in gas-phase, [lb-mol/ft^2·atm·sec]
k_{gw}	mass transfer coefficient of water in gas-phase, [lb-mol/ft^2·atm·sec]
K_L	overall mass transfer coefficient, [ft/sec]

k_L	mass transfer coefficient in liquid-phase, [ft/sec]
L	liquid rate, [GPM]
ℓ	throat length, [mm]
L_m	molar liquid rate, [lb-mol/sec]
L_o	volume liquid rate, [ft^3/sec]
m	specific wetting, [m^3-liquid/m^3-gas]
M_g	mass flow rate of gas, [lb/sec]
M_L	mass flow rate of liquid, [lb/sec]
N_A	rate of SO_2 absorption, [lb-mol/ft^2·sec]
N_{Gr}	Grashof number, $gD_p^3(\rho_g-\rho_g')/\rho_g'\nu_g^2$, [-]
N_{Nu}	Nusselt number, h_gD_p/k, [-]
N_{Pr}	Prandtl number, $C_{pg}\mu_g/k$, [-]
N_{Re}	Reynolds number, $\rho_g\ v_g-v_L\ \cdot D_p/\mu_g$, [-]
N_{Sc}	Schmidt number, μ_g/ρ_gD, [-]
N_{Sh}	Sherwood number, k_cD_p/D, [-]
P	total pressure in venturi, [atm] or[mmHg]
p_{SO_2}	partial pressure of SO_2 in bulk phase of gas, [atm]
$p^*_{SO_2}$	partial pressure of SO_2 at interface, [atm]
p_w	partial pressure of water in bulk phase of gas, [atm]
p^*_w	partial pressure of water at interface, [atm]
q	liquid rate, [liters/m^3]
R	liquid to gas ratio, [gallon/MACF]
r_D	radius of droplet, [ft]
S	cross-sectional area of venturi, [ft^2]

T	absolute temperature, [^{o}R] or[^{o}K]
t	time, [sec]
t_g	temperature of gas, [^{o}F]
t_L	temperature of liquid, [^{o}F]
v_g	velocity of gas, [ft/sec]
v_L	velocity of liquid droplet, [ft/sec]
v_{ro}	relative velocity of gas to liquid at throat, [ft/sec]
v'_{ro}	relative velocity of gas to liquid at throat, [m/sec]
w	gas velocity at throat, [ft/sec]
x	mole fraction of solute in liquid, [-]
y_w	mole fraction of water in gas-phase, [-]
y_w^*	mole fraction of water at interface, [-]
Z	distance along axial direction of venturi, [ft]

Greek Letters

β	heat of vaporization, [Btu/lb-mol]
ΔP_d	friction loss, [N/m^2]
ΔP_1	pressure drop in venturi, [N/m^2]
ΔP_2	pressure drop in venturi, [mmH_2O]
ΔP_3	pressure drop in venturi, [in H_2O]
ε	void fraction in venturi, [-]
μ_g	viscosity of gas, [C.P.] or [lb/ft·sec]
μ_L	viscosity of liquid, [C.P.]
ν_g	kinetic viscosity of gas, [ft^2/sec]
ρ_g	density of gas, [lb/ft^3]
ρ'_g	density of gas without solute, [lb/ft^3]

ρ_L	density of liquid, [lb/ft^3] or [g/m^3]
ρ_M	molar density, [lb-mol/ft^3]
σ	surface tension, [dyne/cm]

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Appendix: Data of SO_2 Absorption by O.A.P. Venturi Scrubber

Run	Gas Temp., °F		SO_2 Conc., PPM		Liquid		Inlet Gas	Pressure Drop
No.	Inlet	Outlet	In	Out (or % removal)		Rate GPM	ACFM	in H_2O
1	310	115	1980	1750	H_2O	10	1037	8.75
1A	320	110	2055	1790	"	10	1087	8.6
2	320	115	2000	1800	"	10	1023	7.8
3	315	110	2050	1780	"	10	1229	12.0
3A	300	100	1993	1705	"	10	1206	11.4
4	310	110	2060	1700	"	15	1006	9.0
5	275	110	1980	1740	"	10	1010	8.5
6	310	110	2000	1160	0.12%NaOH	10	1070	8.4
7	320	115	1980	710	"	15	1051	9.5
I-1A	300	115	2000	(12.85)	H_2O	10	900	8.6
I-2	300	115	2000	(12.60)	"	10	900	7.8
I-3A	300	100	2000	(14.45)	"	10	1100	11.4
I-4	300	110	2000	(17.50)	"	15	900	9.0
I-5	250	110	2000	(12.10)	"	10	900	8.5
I-6	300	115	2000	(42.0)	0.12%NaOH	10	900	8.4
I-7	300	115	2000	(64.2)	"	15	900	9.2
I-8	300	100	2000	(37.9)	"	10	1100	12.4
I-9	250	95	2000	(33.0)	"	10	900	10.2
I-10	300	105	2000	(24.7)	0.045%NaOH	10	900	8.6

MATHEMATICAL MODELS FOR PRESSURE DROP, PARTICULATE REMOVAL AND SO_2 REMOVAL IN VENTURI, TCA AND HYDRO-FILTER SCRUBBERS

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INTRODUCTION

The Office of Air Programs (OAP) is sponsoring a project to fully characterize wet limestone scrubbing for removal of sulfur dioxide and particulates from boiler flue gas in a large prototype system. The test facility consists of three parallel scrubber systems, each capable of treating approximately 30,000 acfm of flue gas, which are integrated into the flue gas ductwork of an existing coal-fired boiler at the TVA Shawnee Power Station. The test facility and test program are described in Ref. 55.

Bechtel Corporation, as the major contractor, is developing mathematical models to characterize the three scrubber systems, in order to allow for effective and economic scale-up to full-size scrubber systems. The model predictions are to be compared with the test facility data and best-fit values for uncertain constants and coefficients calculated.

This paper presents, in abbreviated form, the models which have beed developed to date for pressure drop, particulate removal, and SO_2 removal in the venturi, TCA, and Hydro-Filter scrubbers.

VENTURI SCRUBBER

A venturi scrubber offers the advantages of high particulate removal efficiency (for relatively small particles), mechanical simplicity and proven reliability for slurry systems.

PRESSURE DROP

A number of investigators have developed models for predicting pressure drop in venturi scrubbers (Refs. 1 through 5). Recently, Boll and Leeman (Ref. 1) presented a numeric (computer) solution to the simulataneous differential equations of drop motion and momentum.

Calvert (Ref. 2) has proposed that the velocity head-loss in a venturi is a linear function of liquid-to-gas ratio:

$$\frac{\Delta p}{\Delta (U)^2} = \alpha_0 + \alpha_1 (L/G) \qquad (1)$$

Clavert (Ref. 3) cites a simplified version of the above equation, which is in good agreement with observations reported by McKenna (Ref. 6) on a variable orifice Research Cottrell venturi (Ref. 7).

$$\Delta p = 3 \times 10^{-5} U_t^2 (L/G) \qquad (2)$$

In Figure 1, the Calvert equation is compared with the McKenna data (Ref. 6) and with data from an OAP "in-house" venturi (Ref. 8).

Recently, Wen (Ref. 9) has compared results from the Matrozov (Ref. 4) and Volgin (Ref. 5) correlations for venturi pressure drops with data taken in the OAP venturi. The Matrozov and Volgin equations can be represented by the form:*

$$\Delta p = \beta_1 + \beta_2 U_t^{\beta_3} (L/G)^{\beta_4} \qquad (3)$$

The form of the expression for pressure drop which will be tested with the data obtained at the test facility is given by Eq. 3, where the best values for the constants β_1, through β_4 are to be determined.

PARTICULATE REMOVAL

Various investigators (Refs. 3, 11 and 12) have studies particulate collection in venturis. It seems generally agreed upon that the "inertial impaction" mechanism (Ref. 12) is the important one.

Calvert (Ref. 3) has presented the following correlation for particulate removal in the diverging section of a venturi, based upon impact theory.

$$\eta(i) = 1 - \exp\left[-3.7\times10^{-9}\left(\frac{4 Q_L \rho_L D_0}{55 A_t \mu_G}\right) E_i \frac{(U_t - v_t)}{2 v_t}\right] \qquad (4)$$

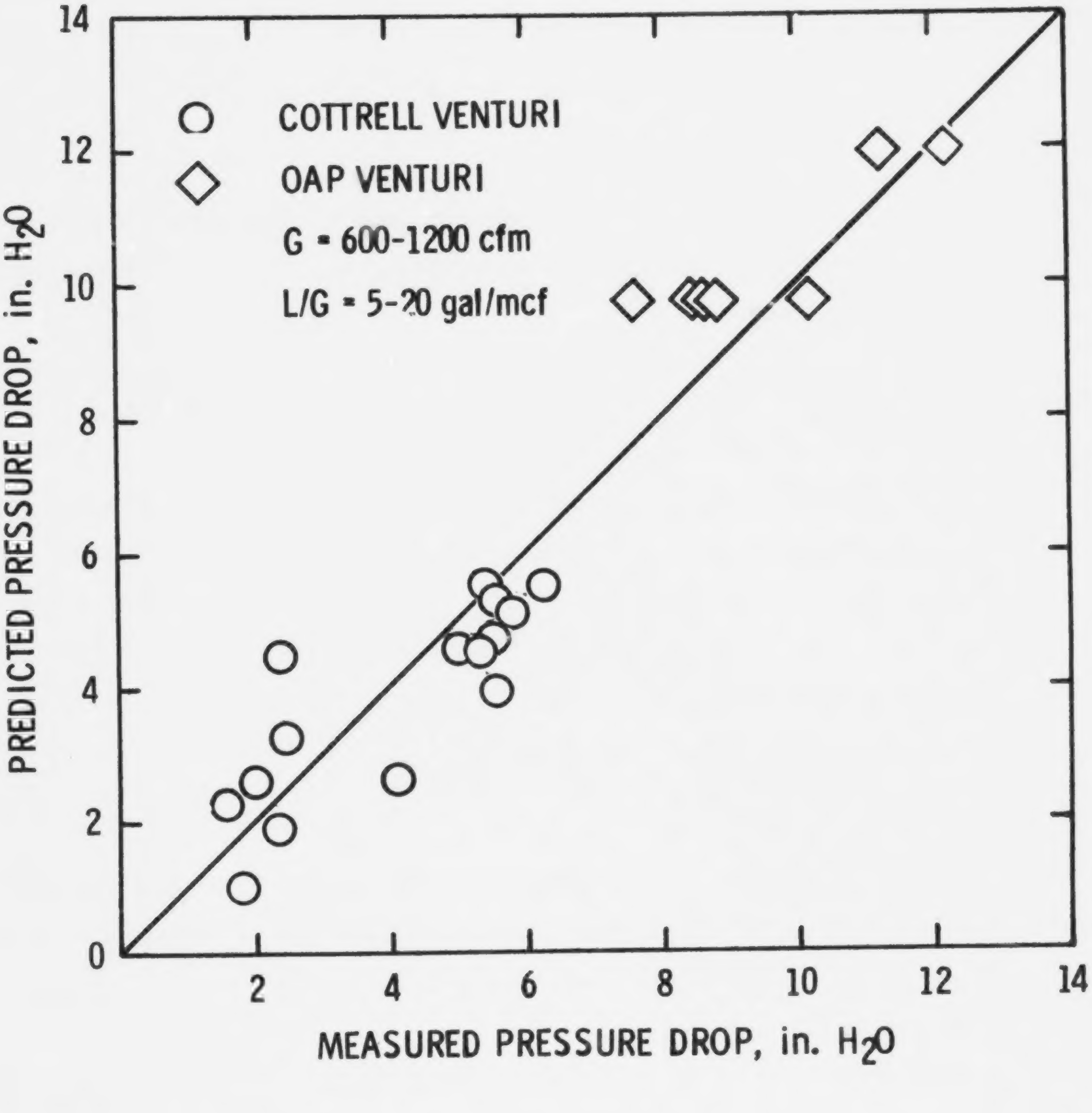
---

* In the Volgin equation $\beta_1 = 0$ and β_2 is a function of venturi geometry. In the Matrozov equation β_1 is a function of venturi geometry.

** The equation for D_0 will be given in the following section on absorption of SO_2.

FIGURE 1

COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF PRESSURE DROP FOR VENTURI SCRUBBERS



The collection efficiency, E_i , which is used in the model, is an approximation of the experimental results of Walton and Woolcock (Ref. 13):

$$E_i = \frac{K_i^2}{(K_i + 0.7)^2} \qquad (5)$$

The inertial impaction parameter, K_i, is defined as:

$$K_i = \frac{3.28 \times 10^{-6} \rho_p U_t d_i^2}{9 \mu_G D_o} \qquad (6)$$

Calvert has found that Eq. 4 agrees with limited experimental data if the velocity ratio, $(U_t - v_t)/v_t$, is set equal to 0.4. With this assumption, Eq. 4 becomes:

$$\eta(i) = 1 - \exp\left[-1.5 \times 10^{-5} (L/G) U_t D_o E_i\right] \qquad (7)$$

The assumed fly ash size distribution curve for the test facility is shown in Figure 2 (Ref. 14). The computer model for predicting particulate removal divides this curve into representative size ranges*, calculates removal efficiencies for each size, then predicts overall collection efficiency.

$$\eta(\text{overall}) = \sum_i \eta(i) W_i \qquad (8)$$

Overall particulate removal efficiencies and pressure drops, are predicted by the Calvert equations (Eqs. 3, 7, and 8), as shown in Figure 3, as a function of liquid and gas flow rates.

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* Size ranges of: 0-1, 1-2, 2-3, 3-6, 6-10, and > 10 microns.

FIGURE 2
TEST FACILITY FLYASH DISTRIBUTION

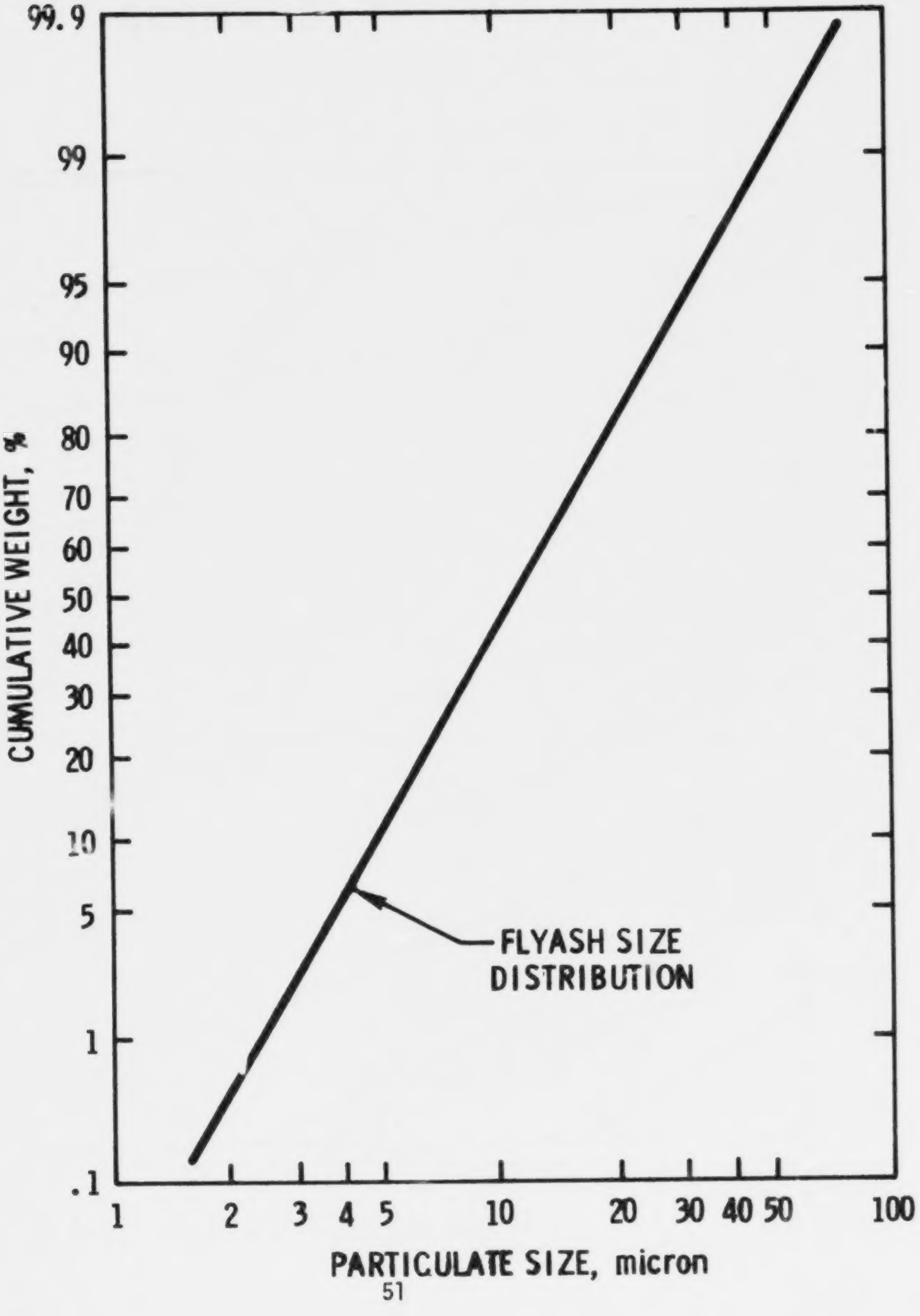
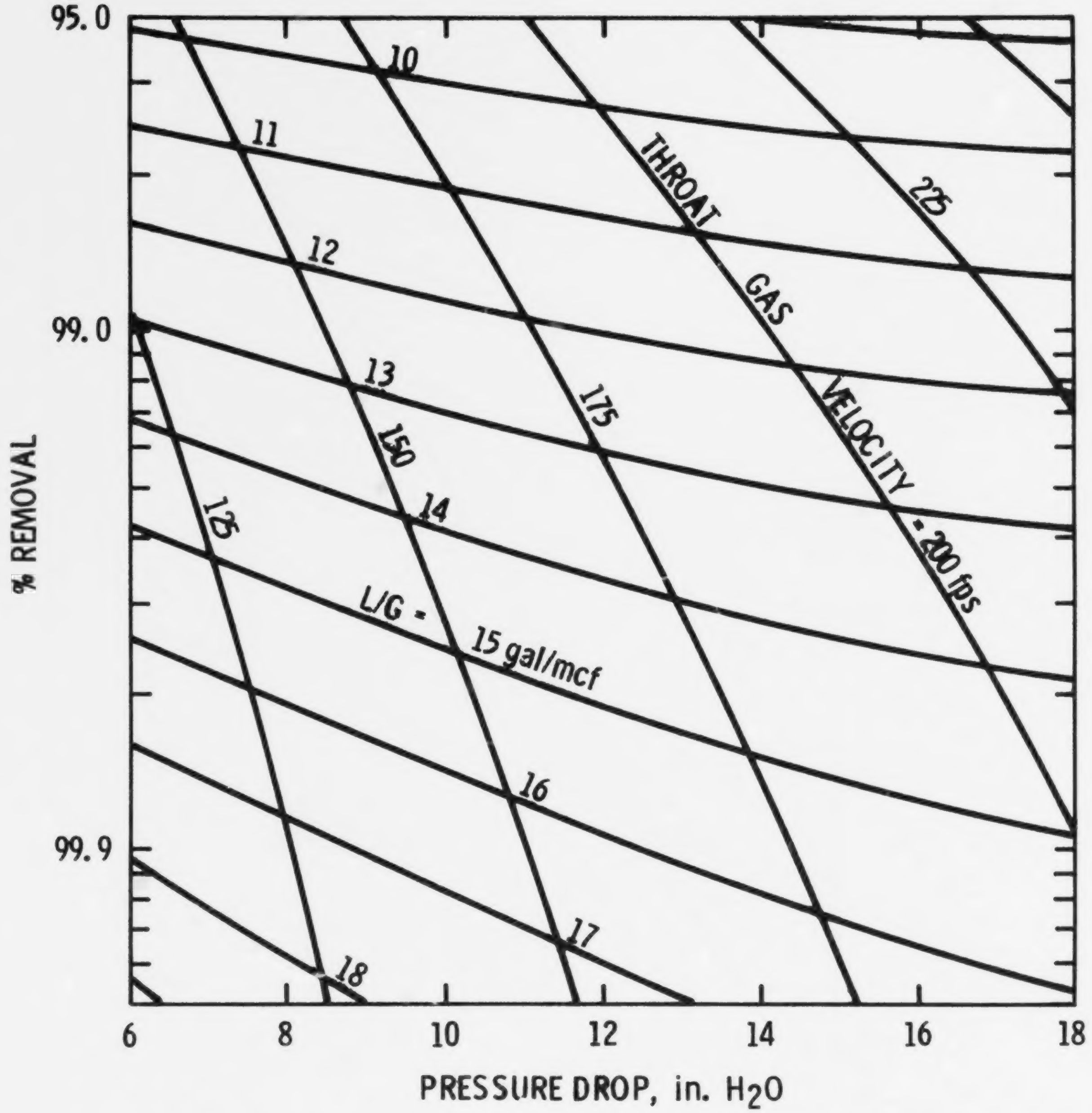


FIGURE 3

PREDICTED VENTURI PARTICULATE REMOVAL AND PRESSURE DROP FROM CALVERT EQUATIONS



In Figure 4, a comparison has been made between predicted (Eqs. 7 and 8) and measure overall particulate removal efficiencies in a Chemico pilot venturi. The data was obtained from tests with flue gas at the Crane Station (Baltimore Gas and Electric) and Dickerson Station (Potomac Electric Power Company), with a 1500 cfm venturi absorber.

The form of the expression for particulate removal which will be tested with the data obtained at the test facility is:

$$\eta(i) = 1 - \exp\left[-\beta_1 (L/G)^{\beta_2} (D_0 U_t)^{\beta_2} E_i\right] \qquad (9)$$

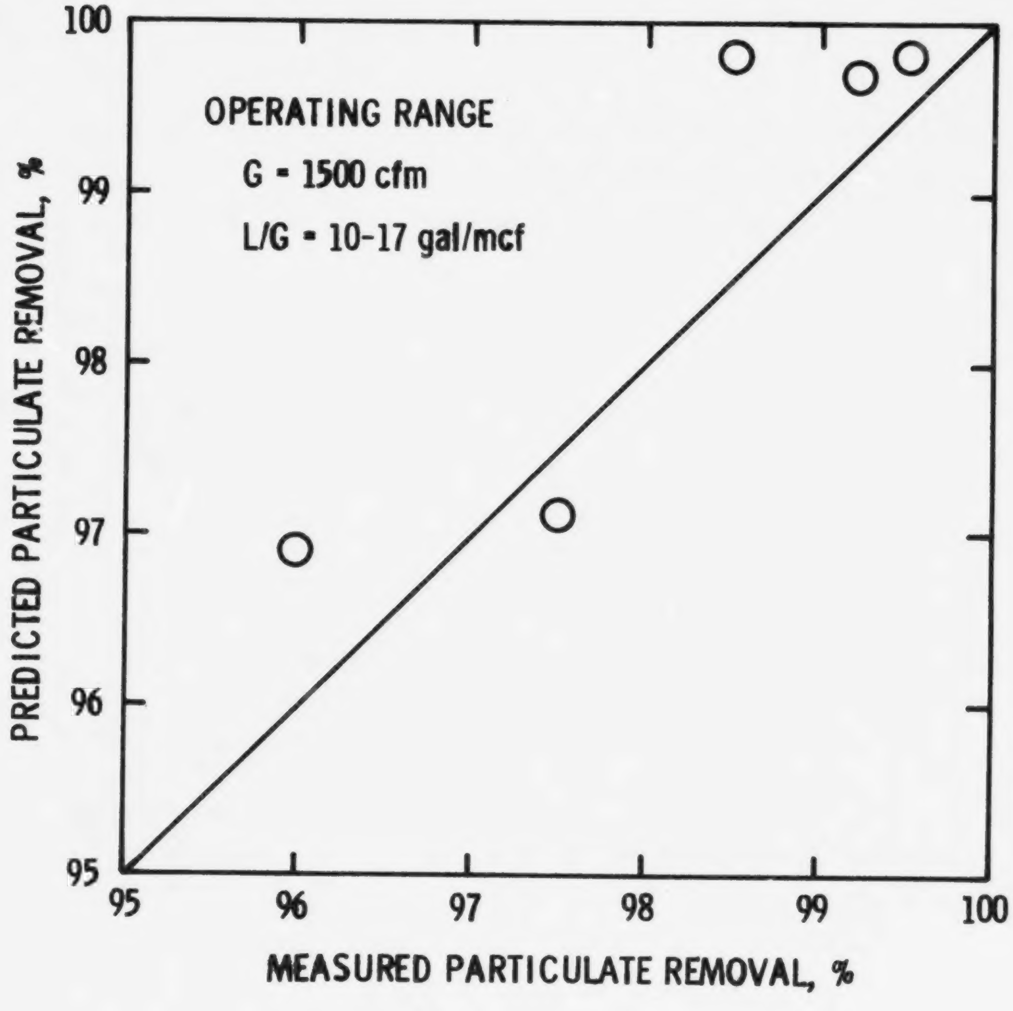
where E_i is obtained from Eq. 5 and the coefficients β_1 and β_2 are to be fitted to the data. The parameter D_0 is to be directly measured from photographic data, if possible.

ABSORPTION OF SULFUR DIOXIDE

The following are the major assumptions made in the formulations of the mathematical models for SO_2 absorption during limestone wet-scrubbing in a venturi:

- The droplets are spherical
- The liquid droplets do not either coalesce or re-shatter after atomization.
- The droplets can be presented as having an average diameter
- The change in droplet diameter due to evaporation is negligible.

FIGURE 4
COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF OVERALL PARTICULATE REMOVAL FOR CHEMICO PILOT VENTURI



The original model for predicting SO_2 removal considered a distribution of sizes of droplets, as predicted by a correlation of Nukiyama and Tanasawa (Ref. 15). Subsequently, it was shown that a model based upon droplets of mean diameter D_o (diameter of a single drop with same surface area to volume ratio as total spray) successfully reproduced the results from the multi-droplet model.

Droplet Size

Recently, Wen (Ref. 9) and Boll and Leeman (Ref. 1) have compared predictions from a number of correlations for average droplet diameter in venturi scrubbers. The present development uses the Nukiyama-Tanasawa equation to predict mean droplet size (Ref. 15):

$$D_o = 3.23\times10^5 \frac{\sqrt{\sigma_L/\rho_L}}{(U_o - v_o)} + 62.8\left(\frac{\mu_L}{\sqrt{\sigma_L \rho_L}}\right)^{0.45} (L/G)^{1.5} \qquad (10)$$

Droplet Velocity

In accordance with the assumptions of constant drop mass and spherical shape, the equation of motion for a droplet downstream of the venturi throat can be written:

$$v\frac{dv}{dz} = g + \frac{3}{4}\,\frac{C_D}{D_o}\,\frac{\rho_G}{\rho_L}(U - v)\,|U - v| \qquad (11)$$

The gas velocity at any point is calculated from:

$$U = Q_G/(A\epsilon) \qquad (12)$$

Void fraction, ϵ , at any point is related to the droplet trajectory by:

$$1-\epsilon = Q_L/(Av) \tag{13}$$

The drag coefficient has experimentally been found to depend upon the drop Reynolds number, Re . The functional relation has been shown by Ingebo (Ref. 16) to be:

$$C_D = 27/Re^{0.84} \tag{14}$$

where

$$Re = \rho_G |U-v| D_0/\mu_G \tag{15}$$

Rabin, et. al. (Ref. 17) have shown that, for droplets accelerated from rest, Eq. 14 is valid only for Re $<$ 60. For Re $>$ 60 they found:

$$C_D = 0.217\, Re^{0.217} \tag{16}$$

Eqs. 11 through 16 are solved numerically (computer) for velocities of droplets as a function of distance downstream from the point of atomization.

Mass Transfer

The liquor-solid mixture entering the scrubber is assumed to be in thermodynamic equilibrium. As the mixture passes through the scrubber the SO_2 (and CO_2) which is adsorbed from the gas reacts with the ionic species present in the liquor and, depending upon the concentrations and equilibria, solid phase material can be either formed or dissolved within the liquor. For alkali wet-scrubbing of flue gas, the assumption has been made that the liquor in the venturi is at all times in equilibrium with an interfacial CO_2 vapor pressure of 0.1 atm of CO_2, i.e. the rate of CO_2 absorption (and desorption) from the flue gas is large.

The thermodynamic equilibria in the following models are obtained from a table based upon results from the Radian Equilibrium Computer Program (Ref. 18).

In accordance with the two-film theory, the equations for removal of SO_2 in a differential element of the venturi may be written as:

$$-G\,dy = K_G a\,(y - y^*)\,dz \qquad (17)$$

where

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L} \qquad (18)$$

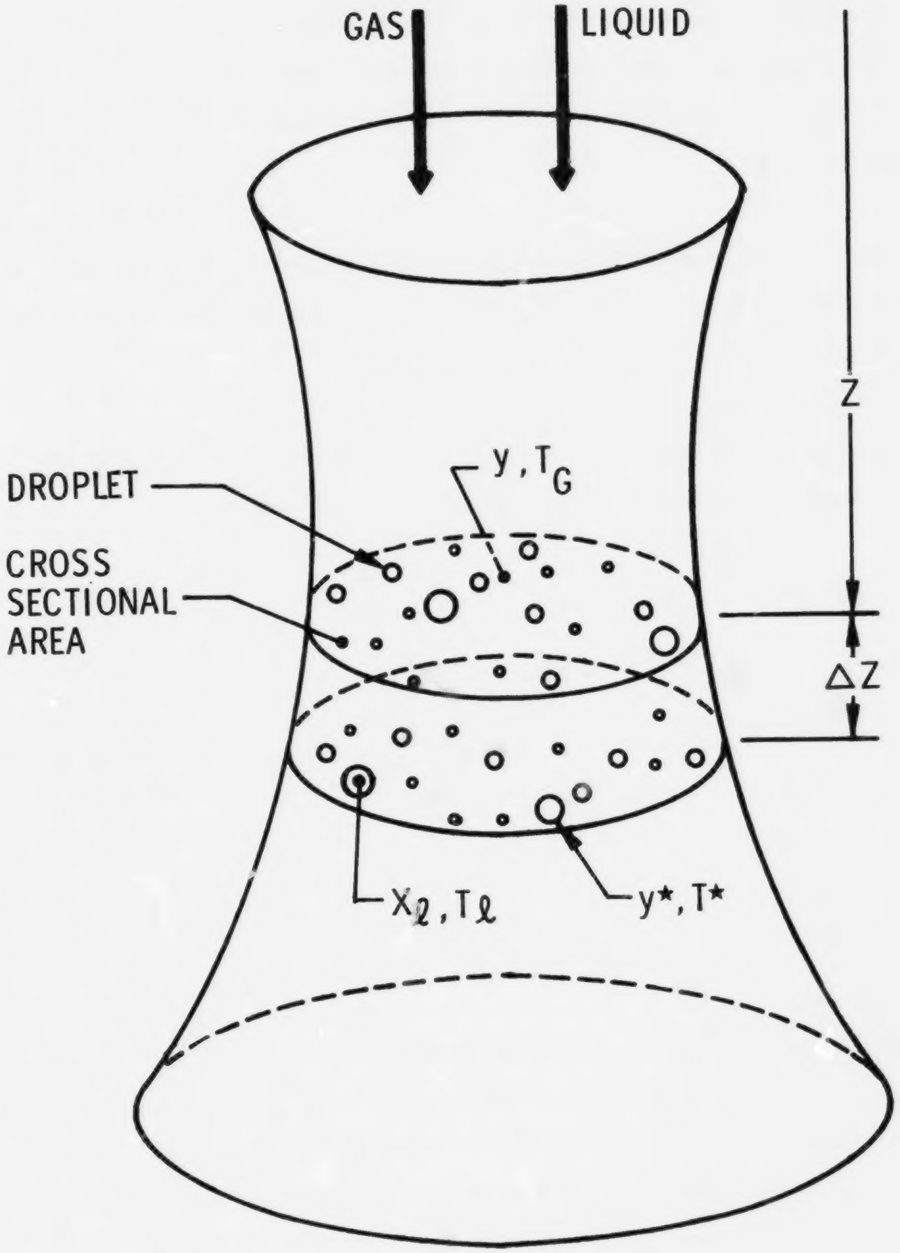
and

$$y^* = m(T^*) \cdot X_{H_2SO_3} \qquad (19)$$

$$X_{H_2SO_3} = \phi\left\{ \vec{X}_{L_0},\ \frac{G C_L}{L}(y - y_0),\ X_S - X_{S_0},\ T_L \right\} \qquad (20)$$

A differential venturi element is shown in Figure 5. Equations 17 through 20 are solved numerically (computer) for SO_2 removal along the venturi axis. The height of the differential elements, Δz, are automatically set within the computer program to give a mathematically stable solution. Equations for predicting interfacial

FIGURE 5
DIFFERENTIAL VENTURI ELEMENT



temperature, T^*, and dissolution of solid species will be presented in the following sections.

Gas and Liquid-Side Mass Transfer Coefficients. The gas-phase mass transfer coefficient is obtained from a correlation developed for mass transfer from gases flowing past single spheres (Ref. 19).

$$Sh = \frac{k_G D_o}{\rho_G \mathscr{D}} = 2 + 0.347\, Re^{0.62}\, Sc^{0.31} \qquad (21)$$

The gas-liquid interfacial area per unit volume is given by:

$$a = 6(1-\epsilon)/D_o \qquad (22)$$

Combining Eqs. 21 and 22 gives:

$$k_G a = \frac{6(1-\epsilon)\rho_G \mathscr{D}}{D_o^2}\left(2 + 0.347\, Re^{0.62}\, Sc^{0.31}\right) \qquad (23)$$

Handlos and Barron (Ref. 20) have presented a correlation for liquid phase mass transfer coefficient (in the absence of chemical reaction) for a "circulating" liquid droplet.

$$k_L^o = \frac{\lambda |U - v|}{768(1 + \mu_L/\mu_G)} \qquad (24)$$

where λ = 2.88 for no continuous phase resistance to mass transfer. Sherwood and Holloway (Ref. 21) and Whitney and Vivian (Ref. 22) determined that temperature had a considerable effect upon liquid-phase mass transfer coefficients. Their results can be summarized as:

$$\frac{k_L @ T_L}{k_L @ 77F} = e^{0.013(T_L - 77)} \qquad (25)$$

Chemical reaction of the absorbed gas in the liquid phase enhances mass transfer by decreasing the bulk liquor composition (and interfacial vapor pressure) of the absorbed gas and by increasing the liquid-film mass transfer coefficient, k_L . Calvert (Ref. 23), Perry (Ref. 24) and Sherwood and Pigford (Ref. 25) have presented reviews of the theories and solutions presently available for determining the effect of chemical reaction on k_L . The analytic results are generally complex and depend upon the rates of reaction, the order of reaction, the rate of diffusion of reactants through the liquid film the concentration of reagents, etc. There is presently, however, no analytic solution available for the case of obsorption followed by a series of reversible homogeneous liquid reactions of varying order and, further complicated, by heterogeneous liquid-solid reactions.

As an example of an approximation to the actual conditions encountered during alkali wet scrubbing of SO_2, consider a very rapid* pseudo-second order irreversible reaction between the dissolved gas A(SO_2)

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* Calvert (Ref. 23) refers to this as the "instantaneous regime". The reaction is so fast that A, the absorbing component, cannot coexist with B, the reacting component. Mass transfer is limited by the diffusion of A and B toward each other to a "reaction plane" where they meet and react (see Figure 4-3, Ref. 23).

and "reagent" B. If the diffusivities of A and B in the liquid are equal, the following expression can be used to predict the effect of reaction upon the liquid-film coefficient (see Refs. 23 and 25):

$$\frac{k_L}{k_L^o} = 1 + \frac{X_B}{\nu X_A} \qquad (26)$$

Combining Eqs. 22, 24, 25, and 26 gives:

$$k_L a = \frac{\lambda \, | U - v |}{76.8 \, (1 + \mu_L / \mu_G)} \left(1 + \frac{X_B}{\nu X_A}\right) e^{0.013 (T_L - 77)} \qquad (27)$$

For alkali wet-scrubbing of flue gas, X_B has been defined as:

$$X_B = X_{CA} + X_{MG} - X_{SO_4} - \tfrac{1}{2} X_{SO_3} \qquad (28)$$

As will be shown in the following section, values for λ and ν of 20 and 1/2, respectively, were obtained by fitting model predictions to pilot plant data.

Heat Transfer

The following set of equations are solved numerically (computer) in each differential element for the interfacial temperature T^* between the liquid droplets and gas, as well as for the gas and droplet temperatures and the evaporation rate of liquid.

$$h_G (T_G - T^*) - h_L (T^* - T_L) = \lambda' K_{WG} (Y^* - Y_G) \qquad (29)$$

$$L \, C_{P_L} \frac{dT_L}{dz} = h_L a (T^* - T_L) \qquad (30)$$

$$G \, C_{PG} \frac{dT_G}{dz} = h_G a (T^* - T_G) \qquad (31)$$

$$-\frac{dL}{dz} = G \frac{dY}{dz} = K_{WG} a (Y^* - Y_G) \qquad (32)$$

A similar type of correlation to Eq. 21 is used to calculate the mass transfer coefficient of water vapor from the droplet surface to the gas. Nusselt-Sherwood analogs are used to calculate h_G and h_L, based on Eqs. 21 and 24, respectively. The correlation of Antoine (Ref. 26) was used to estimate the water vapor pressure at the gas-liquid interface, Y^*.

Dissolution of Solids

The following are the major assumptions made in the formulation of the solids dissolution model. The assumptions only have applicability in that region of operation where the thermodynamic driving force is in the direction of dissolution of solid species.

- The absorbed SO_2 reacts with the dissolved species in solution, resulting in the formation of "reagent" H (hydronium ions) which diffuses through the liquid film surrounding the solid particle and reacts with the solid species S according to:

$$S + \nu H \xrightarrow{k_s} \text{products} \tag{33}$$

- The solid-liquid heterogeneous reactions (Eq. 33) are slow (rate controlling) with respect to liquid phase homogeneous reactions.
- Diffusion of reagent through the liquid film surrounding the solid particle is not rate controlling, i.e. chemical reaction at the solid surface controls.*

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* The data of Smithson and Bakhski (Ref. 27) for dissolution of magnesia (MgO) indicated that chemical reaction was the controlling mechanism. This assumption can be tested by varying liquor temperature during the screening experiments, i.e. if chemical reaction controls, and dissolution rate is measurable, then the rate of dissolution should be a strong (exponential) function of temperature.

- The heterogeneous reaction occurs at the outer skin of a spherical solid particle of radius r. As reaction proceeds the particle dissolves and shrinks in size.* The initial average radius of the particles is R.

- The heterogeneous reaction is first order with respect to H and zero-th order with respect to the solid species.*

The following set of differential equations have been developed, based upon the previous assumptions, for prediction of rate of solids dissolution. The equations have been solved numerically (computer) for each differential scrubber height element, Δz.

$$\frac{dr}{dz} = -\frac{\rho_L(1-\epsilon)}{L}\frac{k_s}{\rho_s}\left(X^*_{CA} - X_{CA}\right) \tag{34}$$

$$\frac{dX_s}{dz} = -\frac{\rho_L(1-\epsilon)}{L}4\pi r^2 k_s N\left(X^*_{CA} - X_{CA}\right) \tag{35}$$

$$\frac{dX_{CA}}{dz} = -\frac{dX_s}{dz} \tag{36}$$

$$X^*_{CA} = \Phi'\left\{\vec{X}_{L0}, X_{S0}, \frac{G\rho_L}{L}(y-y_0), T_L\right\} \tag{37}$$

---

* These assumptions are identical to those made by Levenspiel (Ref. 28) and Wen (Ref. 29).

Initial Conditions

$$r = R \tag{38}$$

$$X_s = X_{so} \tag{39}$$

$$X_{CA} = X_{CAo} \tag{40}$$

Also

$$R = 3/(\rho_s \cdot \gamma_s) \tag{41}$$

$$N = X_{so}/(\rho_s \tfrac{4}{3}\pi R^3) \tag{42}$$

Preliminary venturi results with the dissolution model have indicated that, for values of $k_s \gamma_s X_{so}$ of less than 200 sec^{-1}, the fraction of solids dissolved is essentially zero. For values of $k_s \gamma_s X_{so}$ greater than 1000, the fraction of solids dissolved is approximately equal to the fraction dissolved for an infinite rate of dissolution (the equilibrium dissolution). Therefore, it can be concluded that, there will be essentially zero solids dissolution within the venturi scrubber for initial solids concentrations of less than 200 lb/ft^3 (~ 75% solids) and 20 lb/ft^3 (~ 25% solids), with $k_s \gamma_s$ values of approximately 1 and 10 ft^3/lb sec, respectively.

The data of Smithson and Bakhski (Ref. 27) and the data of Battelle (Ref. 30) indicate that the maximum values for $k_s \gamma_s$ for dissolution of MgO and hydrated limes in an aqueous media is approximately 1 ft^3/lb sec. There is presently no published data for the dissolution of solids in sulfite-bisulfite liquors, from which values of $k_s \gamma_s$ for limes and limestones can be estimated to any degree of accuracy.

Comparison of Predicted SO_2 Removal with Data

Experimental data have been reported by Johnstone and Roberts (Ref. 12), by Johnstone, Field and Tassler (Ref. 10), and by OAP (Ref. 8) for SO_2-sodium and SO_2-water systems. In addition, Cottrell Environmental systems (Ref. 31) has presented results of experiments in which sodium carbonate, lime (CaO), and limestone were employed as the alkali scrubbing agent. The sodium data cover a range of SO_2 removal between less than 10 percent (Ref. 10) and 80 percent (Ref. 12).

For the sodium scrubbing data, it was assumed that the interfacial mole fraction of SO_2, y^*, was zero every where inside the venturi and that the gas phase mass transfer was rate controlling, i.e. $1/k_G \gg m/k_L$.

Johnstone and Roberts: Na_2CO_3 Scrubbing. The experimental venturi of Johnstone and Roberts (Ref. 12) was 4 ft. in length and had a rectangular cross section of 1.5 x 8 inches at the throat. A sodium-water solution was injected at the throat, either as eight vertical jets at the top or as two horizontal jets, one at each side. Gas rates varied between 600 and 1100 cfm corresponding to throat velocities of 140-240 ft/sec. The mole fraction of SO_2 in the inlet gas varied between 800 and 2000 ppm. The range of liquid-to-gas-ratio was 0.7 to 5.5 gal/mcf.

The comparison between predicted and measured SO_2 removals is shown in Figure 6.

Johnstone, Field, and Tassler: NaOH Scrubbing. The experimental venturi geometry of Johnstone, et al (Ref. 10) is shown in Figure 7. These experiments were carried out at very low liquor rates (0.03 to 0.3 gpm) and at relatively high gas throat velocities (500 ft/sec), corresponding to a range of L/G from 0.1 to 1 gal/mcf.

The comparison between predicted and measured SO_2 removal is shown in Figure 8.

OAP In-House Data: Water and NaOH Scrubbing. OAP conducted in-house alkali wet scrubbing experiements in the Cincinnati laboratories of its Division of Process Control Engineering (Ref. 8). Experimental conditions were 1000 cfm of flue gas at 300F containing 2000 ppm SO_2 and 10 to 15 gpm of either water or 0.03 M NaOH solution. The water runs (runs #1, 1a, 2, and 4) are of value in testing the correlation for liquid phase mass transfer coefficients in the absence of chemical reaction (Eq. 24). The usable NaOH runs are those for which gas samples and concentrations were obtained at the venturi exit* (runs #6 and 7).

The OAP venturi is shown in Figure 9. The liquid is sprayed from a 30° nozzle located 3.5 in. in front of the throat. Hence, the liquid droplets and gas are actually in turbulent contact between the nozzle

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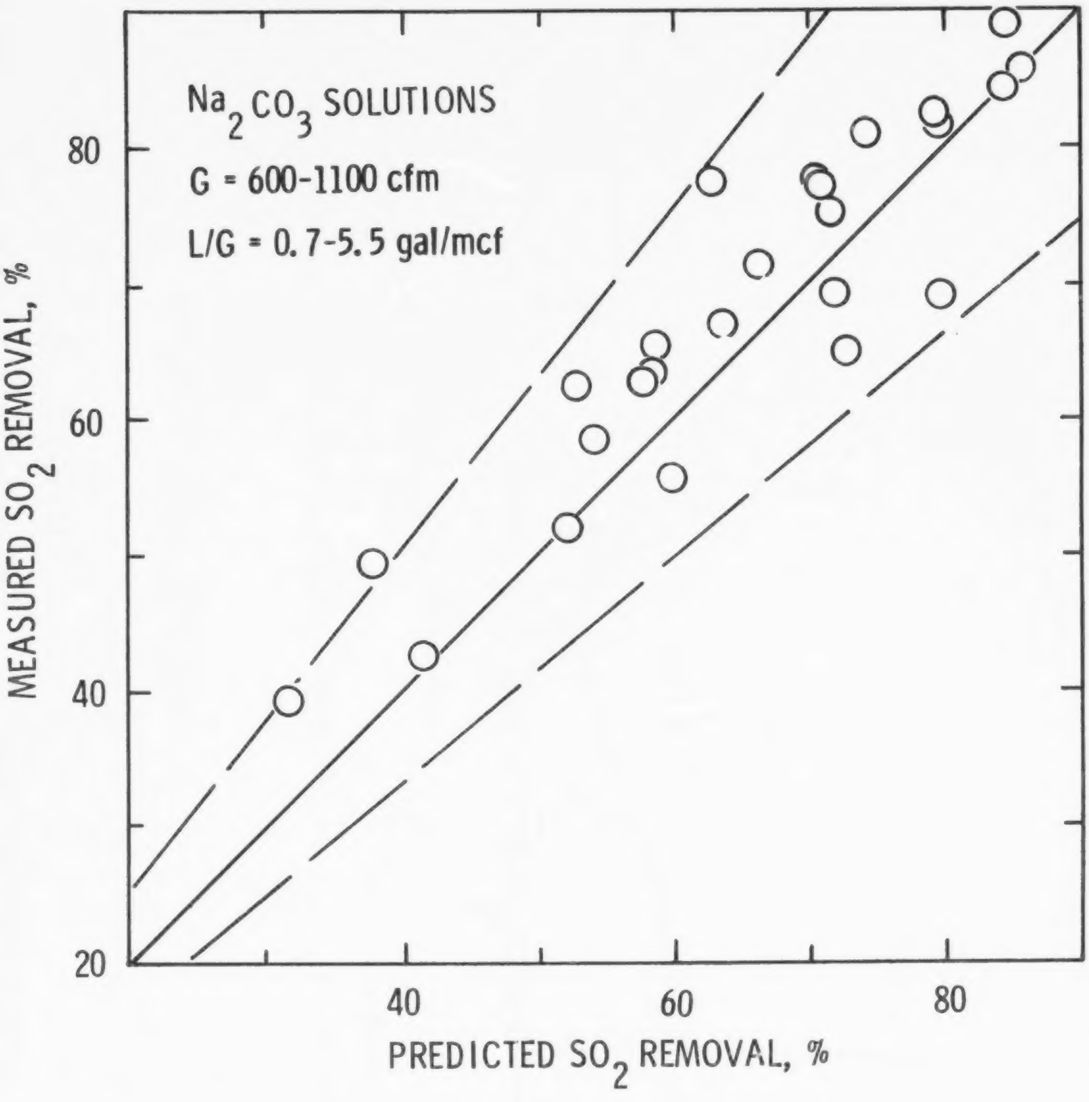
* In all other runs, outlet gas samples were taken only at location several feet downstream of the venturi section, after a knock-out-drum.

FIGURE 6

COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF SO_2 REMOVAL FOR JOHNSTONE-ROBERTS VENTURI



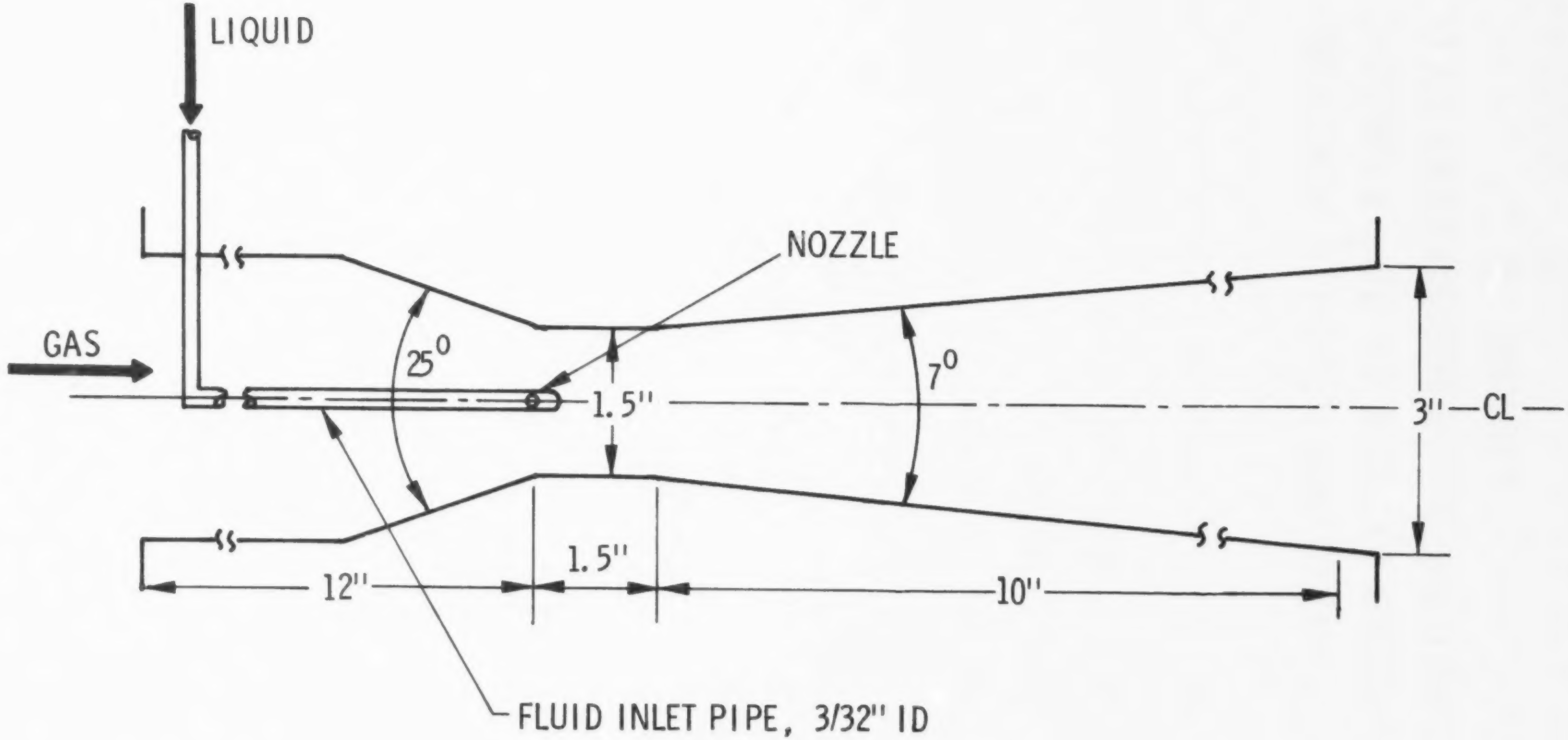
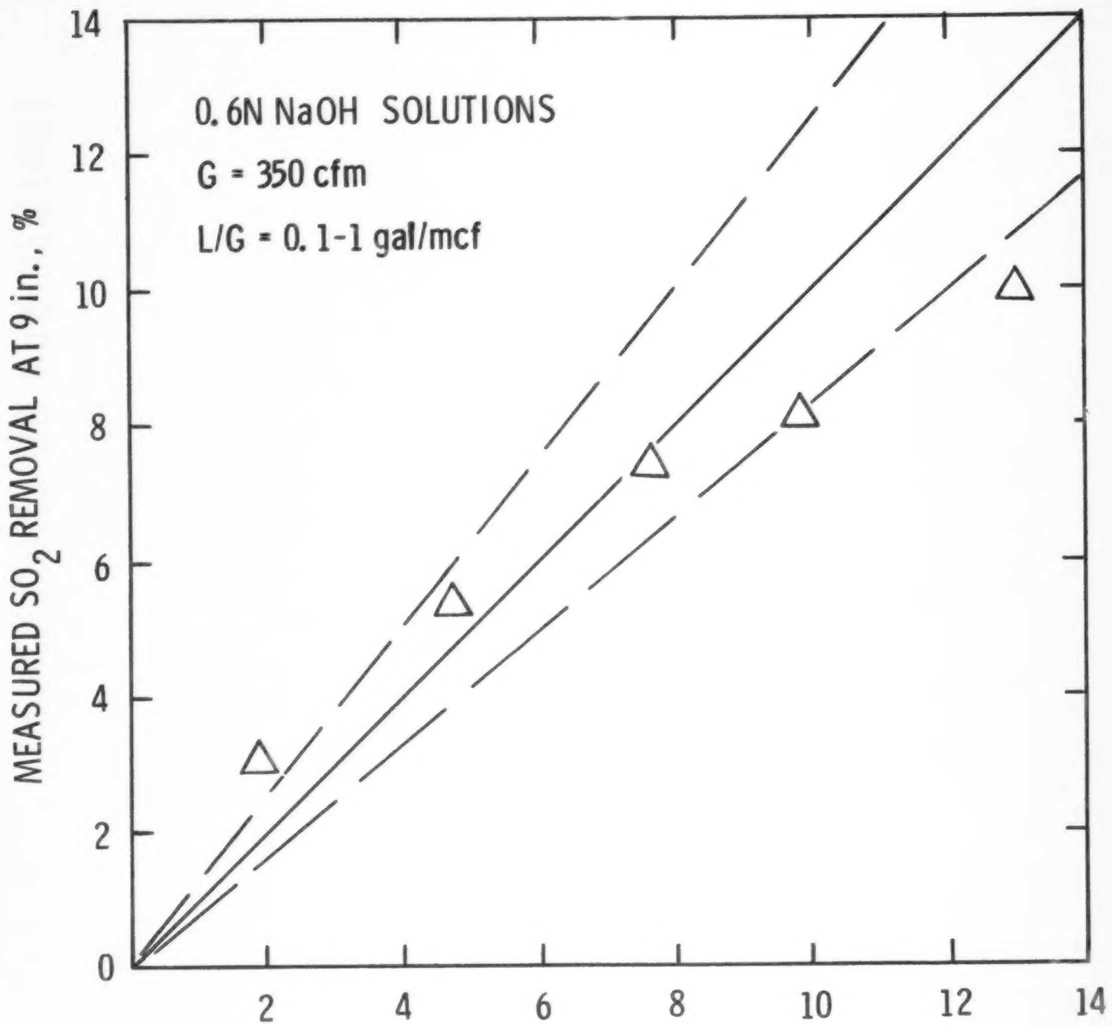


FIGURE 7

DIMENSIONS OF THE JOHNSTONE-FEILD-TASSLER VENTURI

FIGURE 8

COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF SO_2 REMOVAL FOR JOHNSTONE-FEILD-TASSLER VENTURI



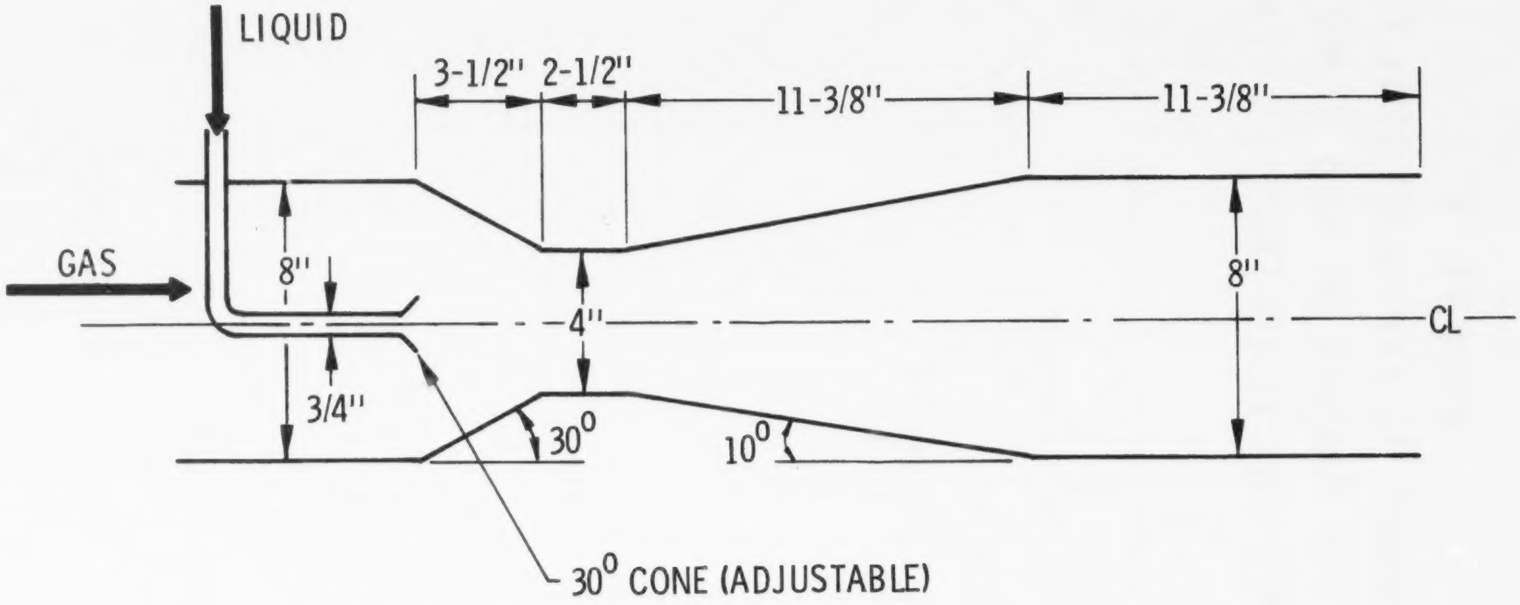


FIGURE 9
DIMENSIONS OF OAP VENTURI

and the throat, and mass transfer occurs in this region. The predictions of the venturi model were accordingly based upon droplet formation at the nozzle.

In Figure 10, model predictions are compared with the water and NaOH solution OAP data. For the NaOH comparisons, the average droplet diameter at the nozzle exit, as predicted by the Nukiyama-Tanasawa correlation (Eq. 9), was reduced by 30%, in order to give a reasonable fit.

For the water runs, a good fit to the data was obtained by using a value of $\lambda = 20$, for the Handlos and Baron correlations for liquid side mass transfer coefficient (Eq. 24). This compares to a value of 2.9 suggested by the authors. For these runs, the predicted SO_2 concentrations in the liquid and gas phases were close to equilibrium near the exit of the venturi. Hence, only a lower limit for the value of λ was obtained.

Profiles of the calculated overall and individual mass transfer coefficients for an OAP water run are presented in Figure 11. Although the liquid phase resistance, m/k_L, is greater than the gas phase resistance, $1/k_G$, neither can be neglected. These results are in agreement with those of Whitney and Vivian (Ref. 22), who studied absorption of SO_2 in water in one-inch ceramic ring packages at 70°F.

Cottrell (Tidd) Data: Na_2CO_3 Scrubbing. In a pilot plant operation at the Tidd Power Station of Ohio Power, Research — Cottrell (Ref. 31) obtained experimental data for SO_2 removal in Na_2CO_3 solutions for

FIGURE 10
COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF SO_2 REMOVAL FOR OAP VENTURI

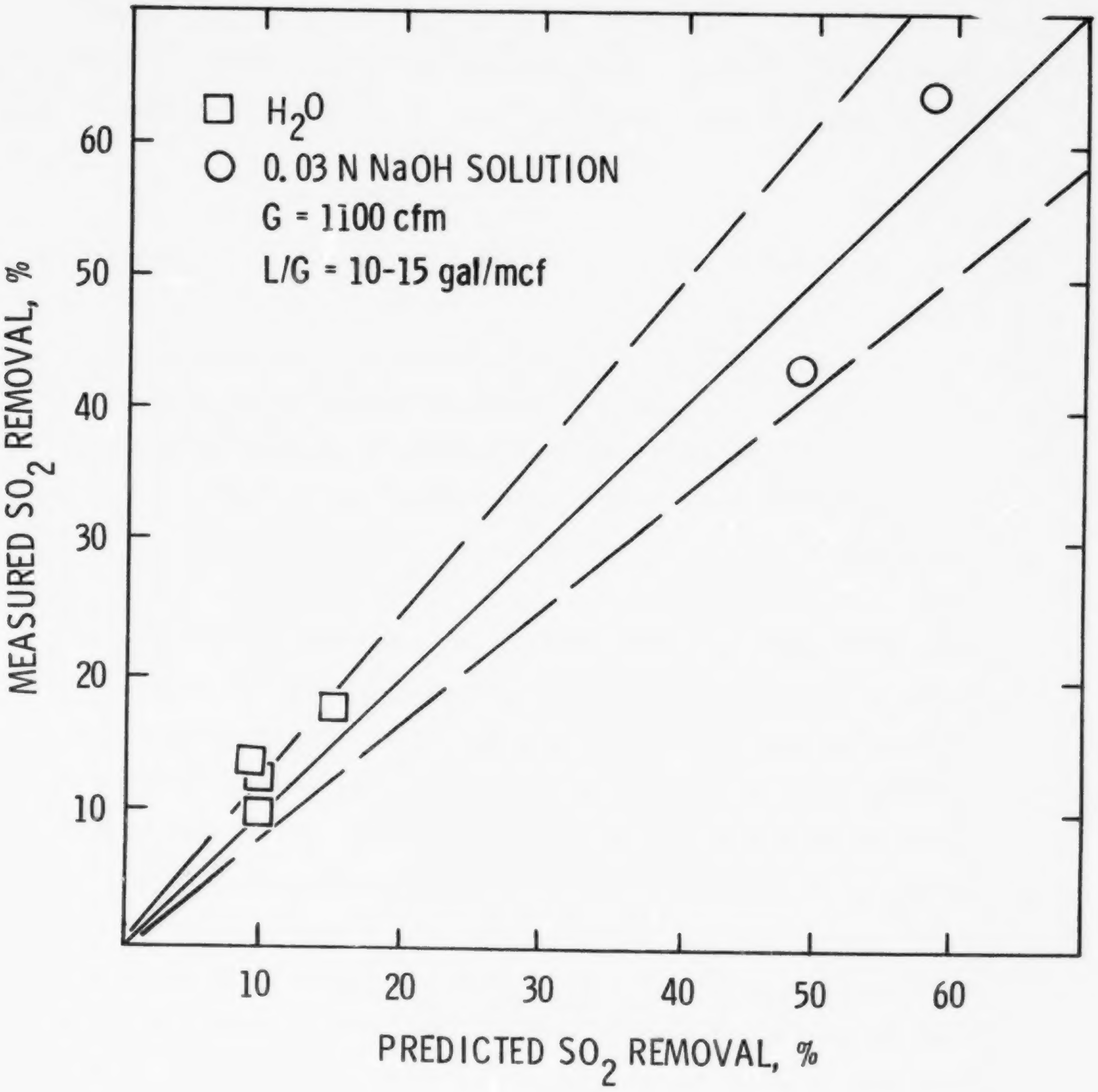
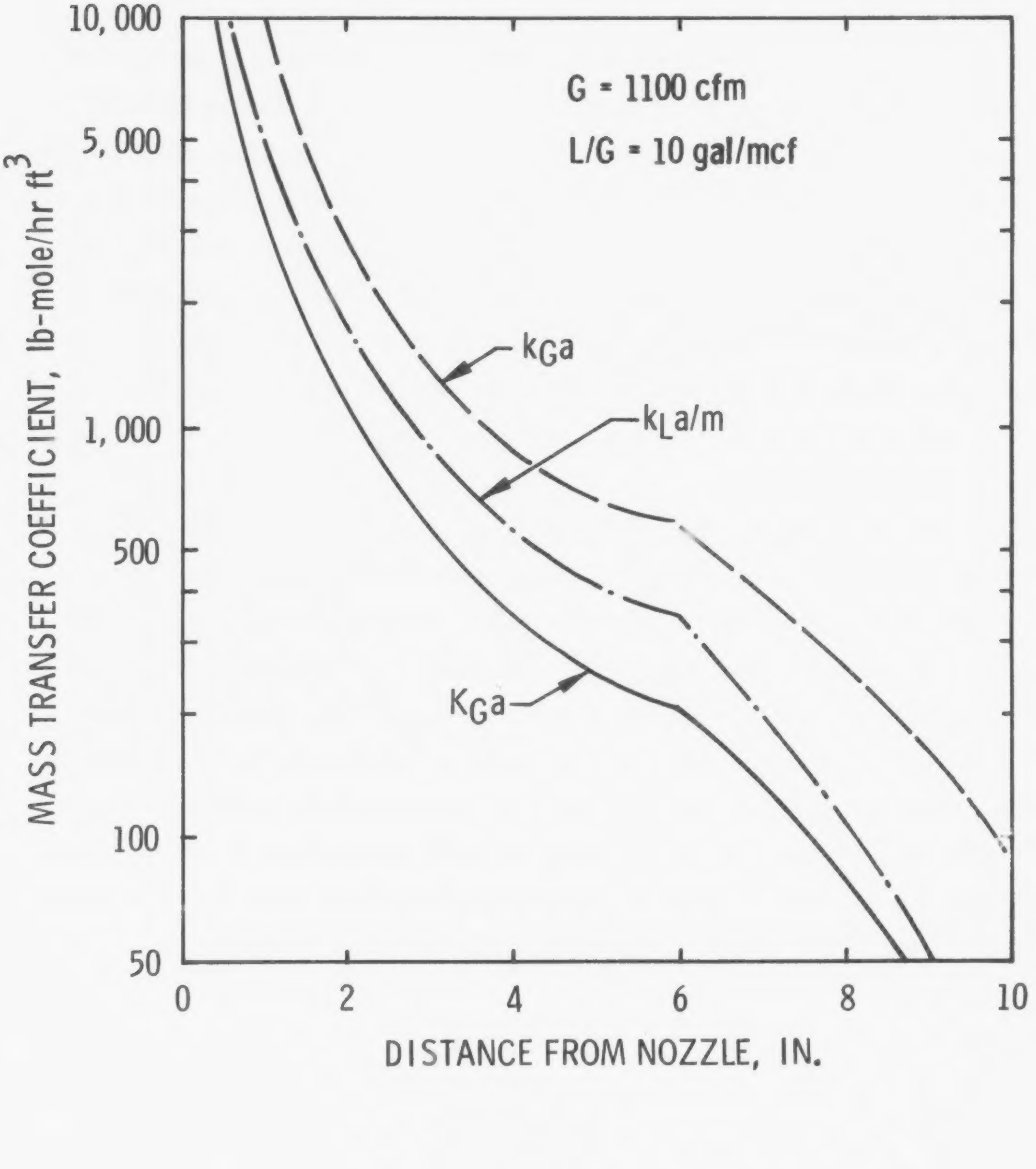


FIGURE 11

PREDICTED MASS TRANSFER COEFFICIENTS FOR SO_2 REMOVAL IN WATER IN OAP VENTURI



a venturi system operated over a wide range of conditions. Flue gas rates were between 300 and 920 cfm and liquor rates varied from 4 to 12 gpm. The Cottrell venturi, which contains an adjustable "flooded disc" is shown in Figure 12.

As was the case for the OAP venturi, the predictions of the model for the Cottrell venturi were based upon droplet formation at the initial point of intimate turbulent contact between liquid and gas, which was assumed to be the point 14 inches downstream from the liquid inlet (see Figure 12). As little mass transfer was expected beyond a bend in the line, located 2.5 ft below the open position of the flooded disc, the model's calculations were terminated at that point. The SO_2 removals predicted by the model are compared with the experimental data in Figure 13. Although these predictions tend to be high for low SO_2 removal and low for high removal, more than three-fourths of the data points are within 20 percent of predicted values.

Cottrell (Tidd) Data: CaO Scrubbing. For the Cottrell experiments in which the SO_2 was removed using lime slurries, there was some dissolution of solid CaO in the scrubber. This was demonstrated by the relatively low removals (13-15 percent) obtained in three experimental runs (Task VII-C) for which a clarified lime solution was sent to the venturi. Since experimental data is lacking for the lime dissolution reaction rate constant and specific surface area, only the three clarified solution runs were compared with predictions from the model. These runs are of interest because they provide an opportunity to examine the predicted effect of chemical reaction in the correlation for k_L

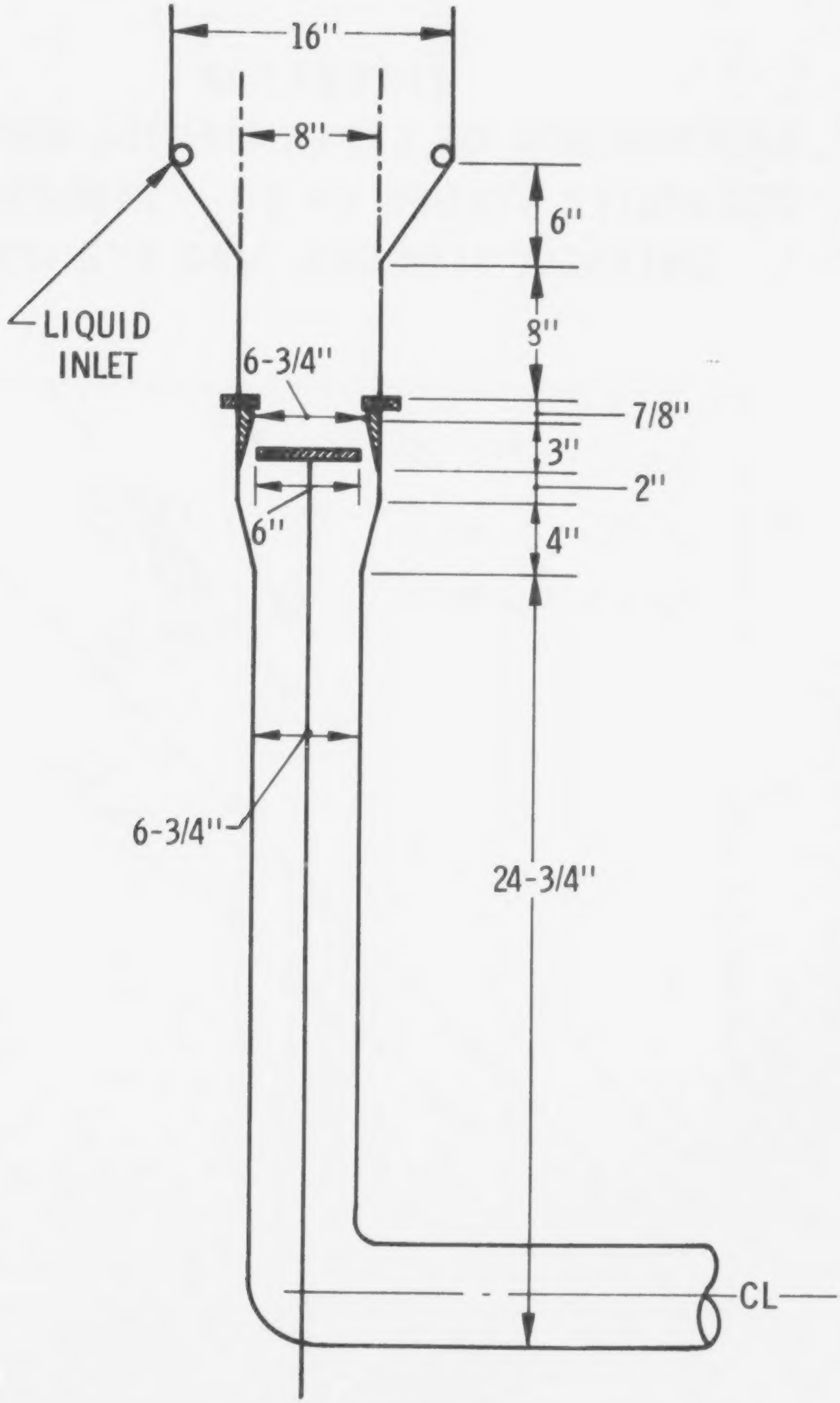
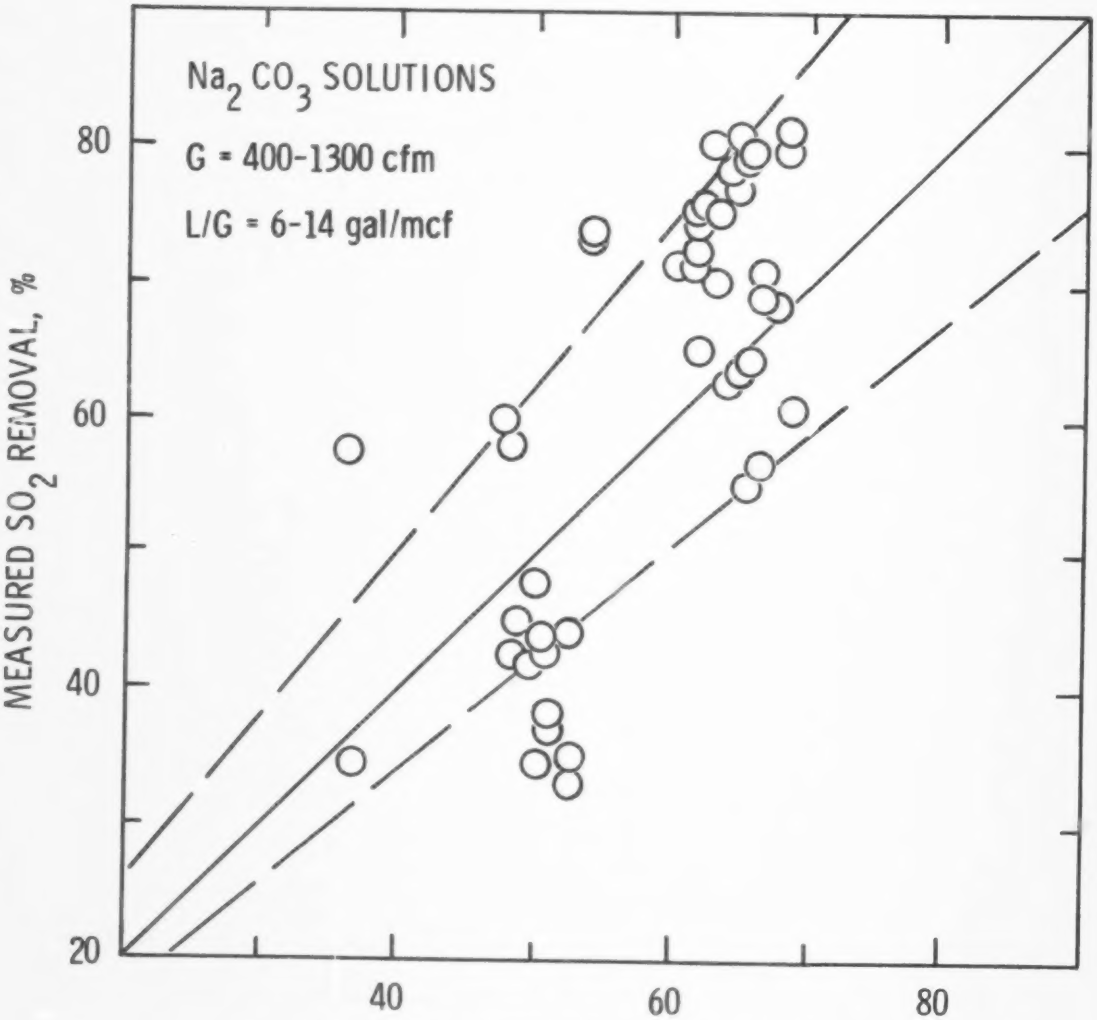


FIGURE 12
DIMENSIONS OF
COTTRELL FLOODED DISC SCRUBBER

FIGURE 13

COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF SO_2 REMOVAL FOR COTTRELL FLOODED DISC SCRUBBER



(see Eqs. 26 and 28). As the outlet liquor pH readings for the clarified lime runs were fairly low (5.2 in each case), the equilibrium interfacial mole fraction of SO_2, y^*, could not be assumed zero. Values for y^* at each axial location were obtained from the table based upon Radian Equilibrium Computer Program.

For three clarified lime runs, the gas rate was maintained at 700 cfm and the liquid-to-gas ratio at 10 gal/mcf. The inlet gas was at a temperature of 330°F and contained approximately 1600 ppm SO_2. Throat velocities were 105 ft/sec.

As Figure 14 indicates, a reasonable correspondence is obtained between predicted and experimental values of SO_2 removal with values of λ and ν in the correlation for k_L (Eq. 27) of 20 and 1/2, respectively. Since the predicted SO_2 concentrations in the gas and liquid were near equilibrium at the exit of the venturi, only (as with the OAP water data) the lower limit for λ (and ν) could be checked.

Profiles of the predicted overall and individual mass transfer coefficients for a clarified lime run are shown in Figure 15. The predicted overall mass transfer coefficient is gas phase controlled for only a short distance after droplet formation. However, about two-thirds of the calculated mass transfer occurs in this region, due to the rapid approach to equilibrium in the absence of appreciable liquid phase resistance. The sharp drop in liquid side coefficient is due to the sudden depletion of "reagent" within the liquid (see Eq. 28).

FIGURE 14
COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF SO_2 REMOVAL FOR COTTRELL FLOODED DISC SCRUBBER

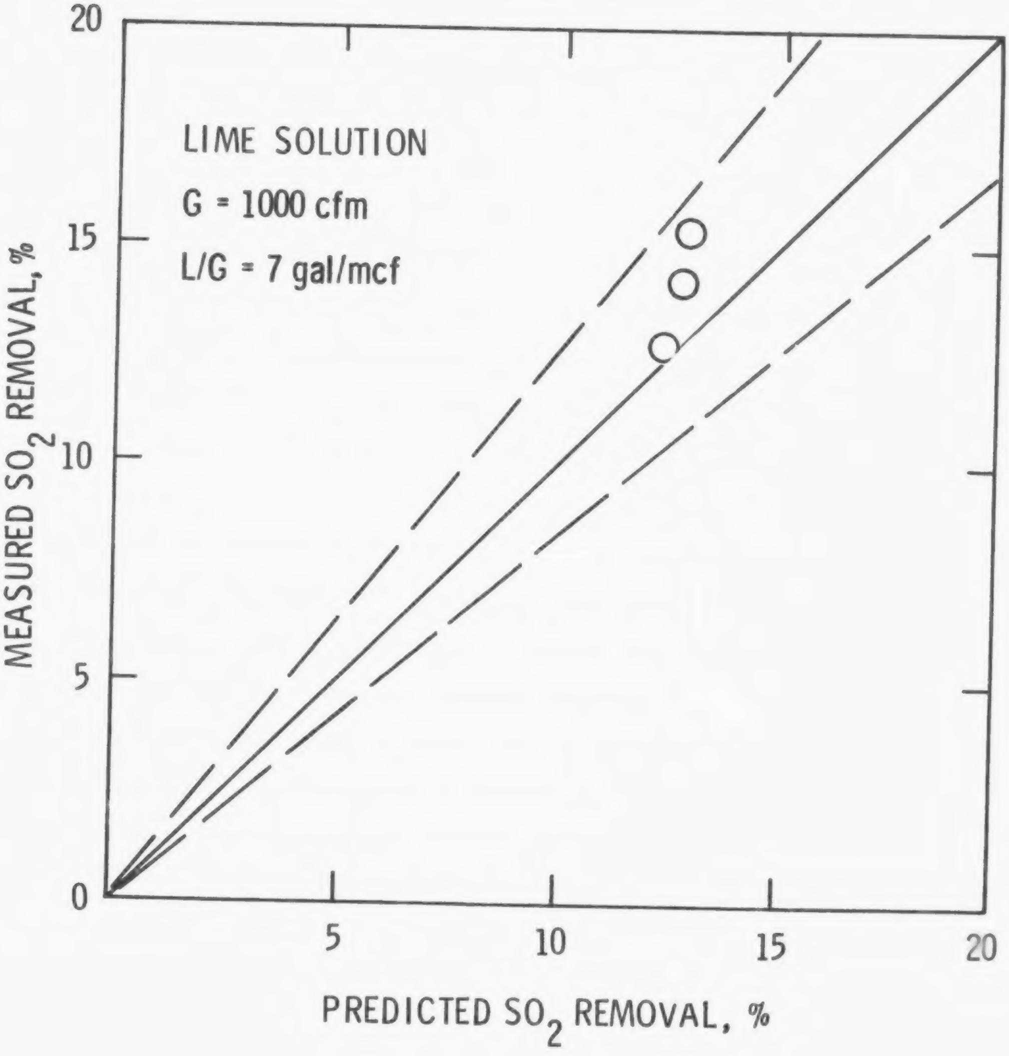
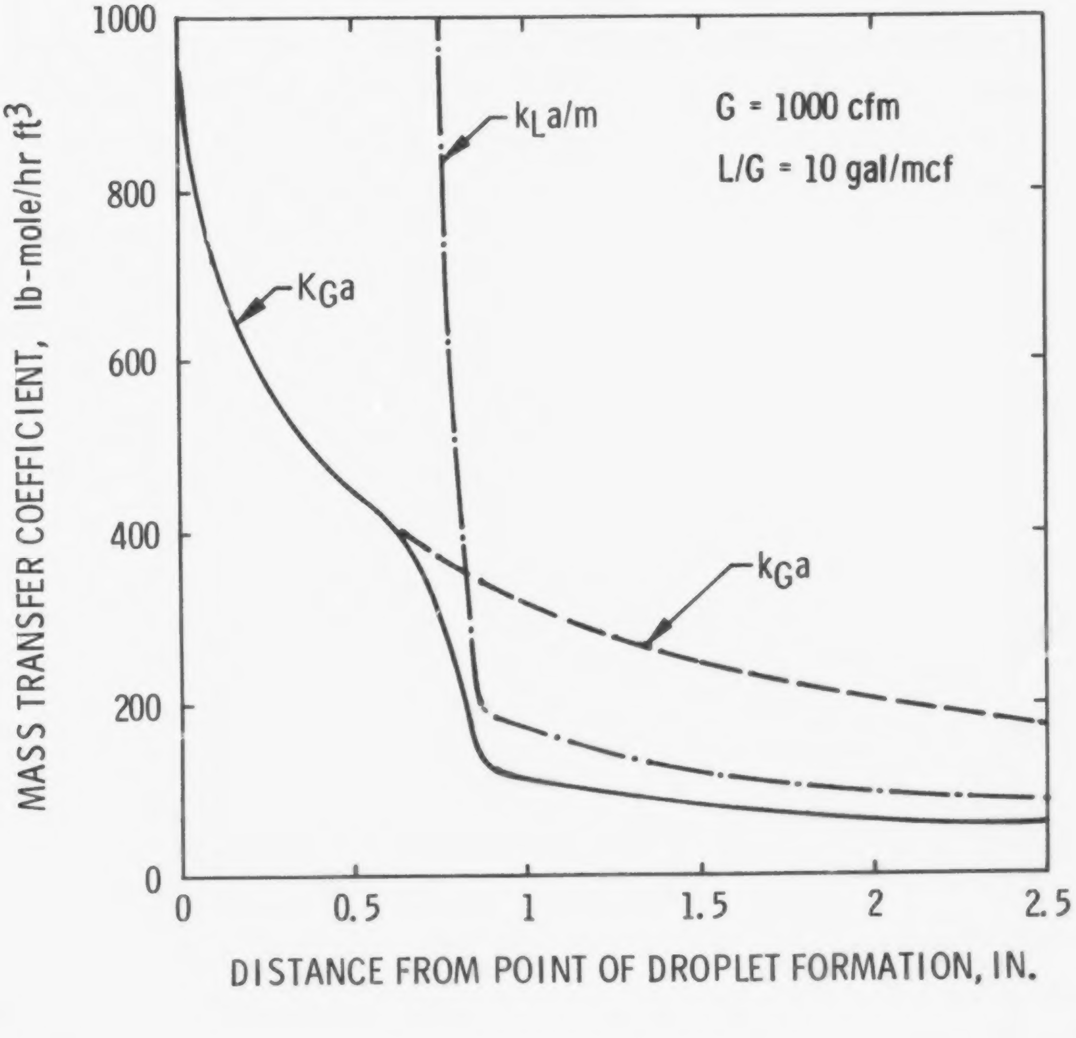


FIGURE 15
PREDICTED MASS TRANSFER COEFFICIENTS FOR SO_2 REMOVAL IN LIME SOLUTION IN COTTRELL FLOODED DISC SCRUBBER

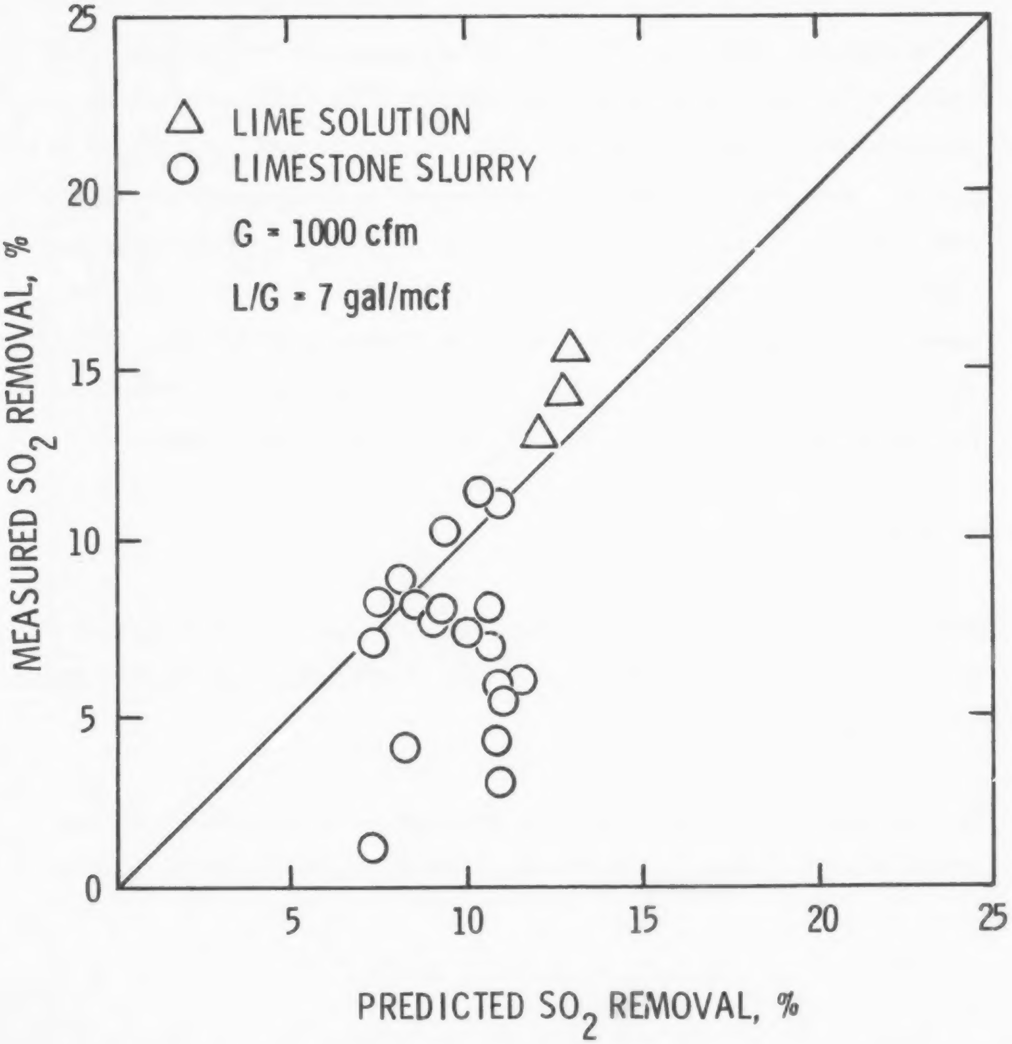


Cottrell (Tidd) Data: Limestone Scrubbing. Of the limestone wet scrubbing experiments conducted by Cottrell at the Tidd pilot plant, only those from Task C-6 are considered to be reliable (Ref. 33). Except for slightly higher gas throat velocities (127 to 151 ft/sec), experimental conditions for these tests were essentially the same as those listed for the clarified lime solution runs in the previous section.

For the model comparisons, the initial liquor compositions were based upon measurements by Radian Corporation during Task C-6 (Ref. 32), with appropriate modification for inlet pH variation from run-to-run. The previously determined values of λ and ν (of 20 and 1/2, respectively) were used in the liquid-side mass transfer coefficient correlation (Eq. 27) and the assumption was made that there was *no solids dissolution.* In Figure 16 the experimental SO_2 removals for limestone wet-scrubbing are compared with the model predictions (the clarified lime runs are also included for comparison). Since, for these limestone runs, the SO_2 measurement error of about ± 160 ppm (see Ref. 31) is as large as the measured removal, the overall comparison is not bad. If an infinite rate of solids dissolution had been assumed, the venturi model would have predicted SO_2 removals of greater than 50% for all of the runs.

FIGURE 16

COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF SO_2 REMOVAL FOR COTTRELL FLOODED DISC SCRUBBER



HYDRO-FILTER SCRUBBER

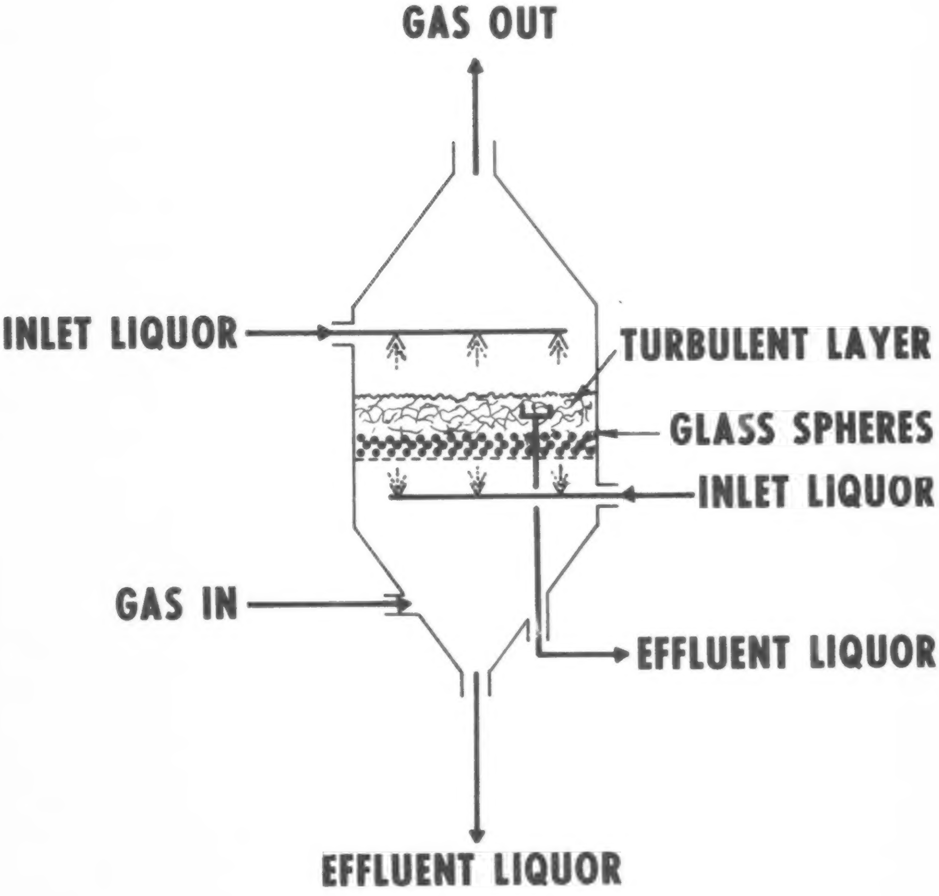
The Hydro-Filter (or flooded-bed) scrubber is shown schematically in Figure 17 and is described in Refs. 34 and 35. Normal operation is as follows: The main liquor stream (plus suspended solids) is sprayed through nozzles onto the bottom side of a bed of glass spheres (marbles); simultaneously, a secondary flow of liquor is sprayed onto the top side of a "turbulent layer" formed above the spheres. Gas (with suspended solids) enters the scrubber at the bottom, concurrently contacts the main liquor stream, bubbles upward through the turbulent layer, and leaves at the top. The main effluent liquor stream is collected in an overflow-weir within the turbulent layer region and is directed out of the scrubber.

PRESSURE DROP

The total gas-phase pressure drop is assumed to be the sum of the pressure drop through the glass-sphere and turbulent-layer regions of the Hydro-Filter.

The pressure drop through the glass-sphere region of the Hydro-Filter may be estimated from the following correlation, which is

FIGURE 17
SCHEMATIC OF HYDRO-FILTER SCRUBBER



based upon the work of Leva (Ref. 36)* and Ergun (Ref. 37).

$$\left(\frac{\Delta p}{z}\right)_M = \frac{1.75\,\frac{1}{2}\,C_f'\,G^2}{6\,g_c'\,\rho_G}\exp\left[\beta(L/G)G^2\right] \qquad (45)$$

where β is a constant which depends upon the type of packing. The characterization factor of packing is given by:

$$C_f' = \frac{6(1-\epsilon)}{\epsilon^3 d_M} \qquad (46)$$

The upper limit on pressure drop occurs when the bed becomes fully fluidized, and it has been suggested by Fan (Ref. 38) and Leva (Ref. 39) that at this point the pressure drop is approximately equal to the weight of the bed. Therefore:

$$\left(\frac{\Delta p}{z}\right)_M \leq \frac{\rho_M(1-\epsilon)}{5.2} \qquad (47)$$

The pressure drop due to the turbulent layer above the spheres is estimated from the following correlation given by Ludwig (Ref. 40):

$$\Delta p_T = 0.75 + 0.375\,H_T \qquad (48)$$

---

[*] It has been assumed that the form of the Leva correlation (Ref. 36), which is based upon data taken below the flooding-line for dumped packings and with countercurrent flow, is applicable for the glass-sphere region of the Hydro-Filter. In normal operation the glass-sphere section is within the flooded range of fixed beds and approaches fluidization. Also, the flow through the spheres is primarily cocurrent.

It follows that the total pressure drop Δp in the Hydro-Filter is given by:

$$\Delta p = H_M \left(\frac{\Delta p}{z} \right)_M + \Delta p_T \qquad (49)$$

The constant β in Eq. 45 was estimated to be 1.5×10^{-8} from a fit of overall pressure drop (Eq. 49) to Hydro-Filter vendor test data (Ref. 41). The comparison between predicted and measured overall pressure drop is shown in Figure 18. For the fitted value of β, Eq. 49 becomes:

$$\Delta p = \frac{1.75 \frac{1}{2} C_f' G^2 H_M}{6 g_c' \rho_G} \exp\left[1.5 \times 10^{-8} (L/G) G^2\right] + 0.75 + 0.375 H_T \qquad (50)$$

In Figure 19 the total predicted pressure drop in the Hydro-Filter (Eq. 50) is shown as a function of the liquid and gas rates.

The form of the expression for pressure drop which will be tested with the data obtained at the facility is:

$$\Delta p = \frac{\beta_1 \frac{1}{2} C_f' G^2 H_M}{6 g_c' \rho_G} \exp\left[\beta_2 (L/G)^{\beta_3} G^2\right] + \beta_5 + \beta_6 H_T \qquad (51)$$

where the coefficients β_1 through β_6 are to be determined from the data.

FIGURE 18
COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF PRESSURE DROP FOR HYDRO-FILTER

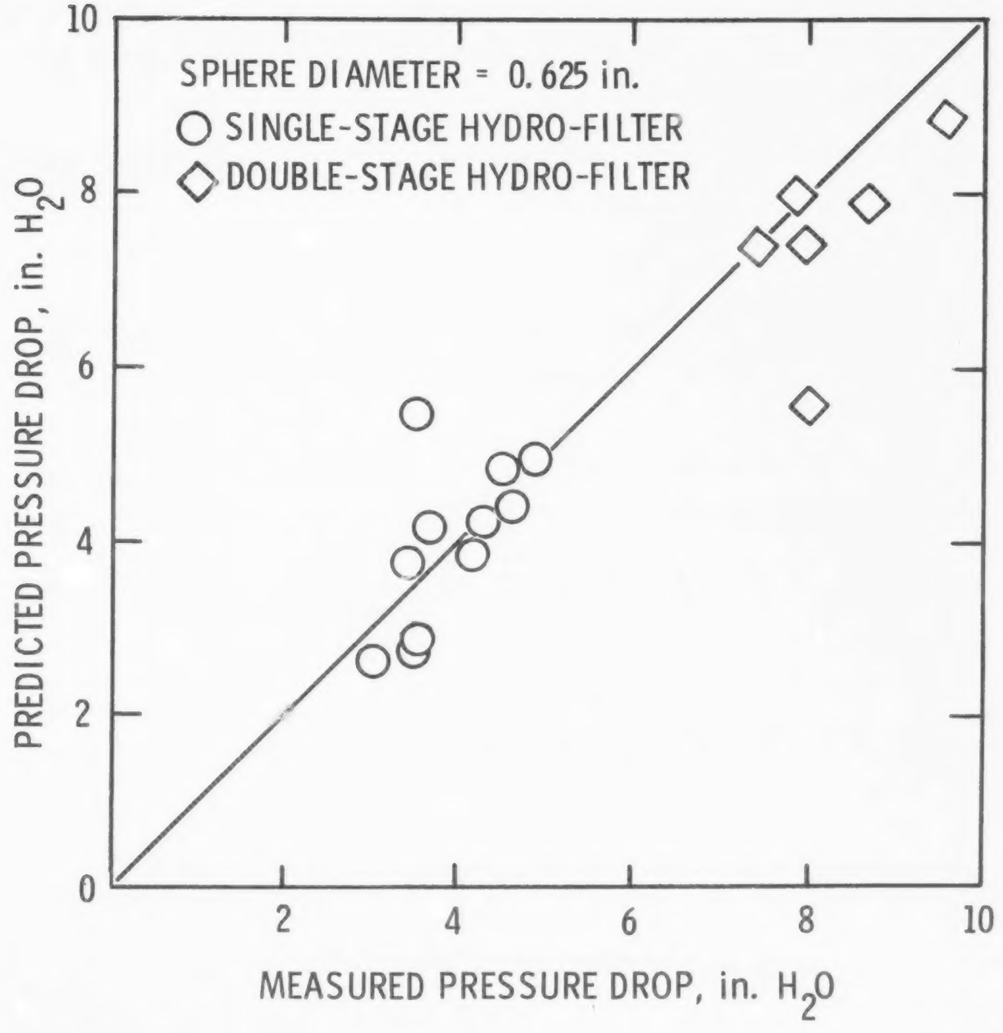
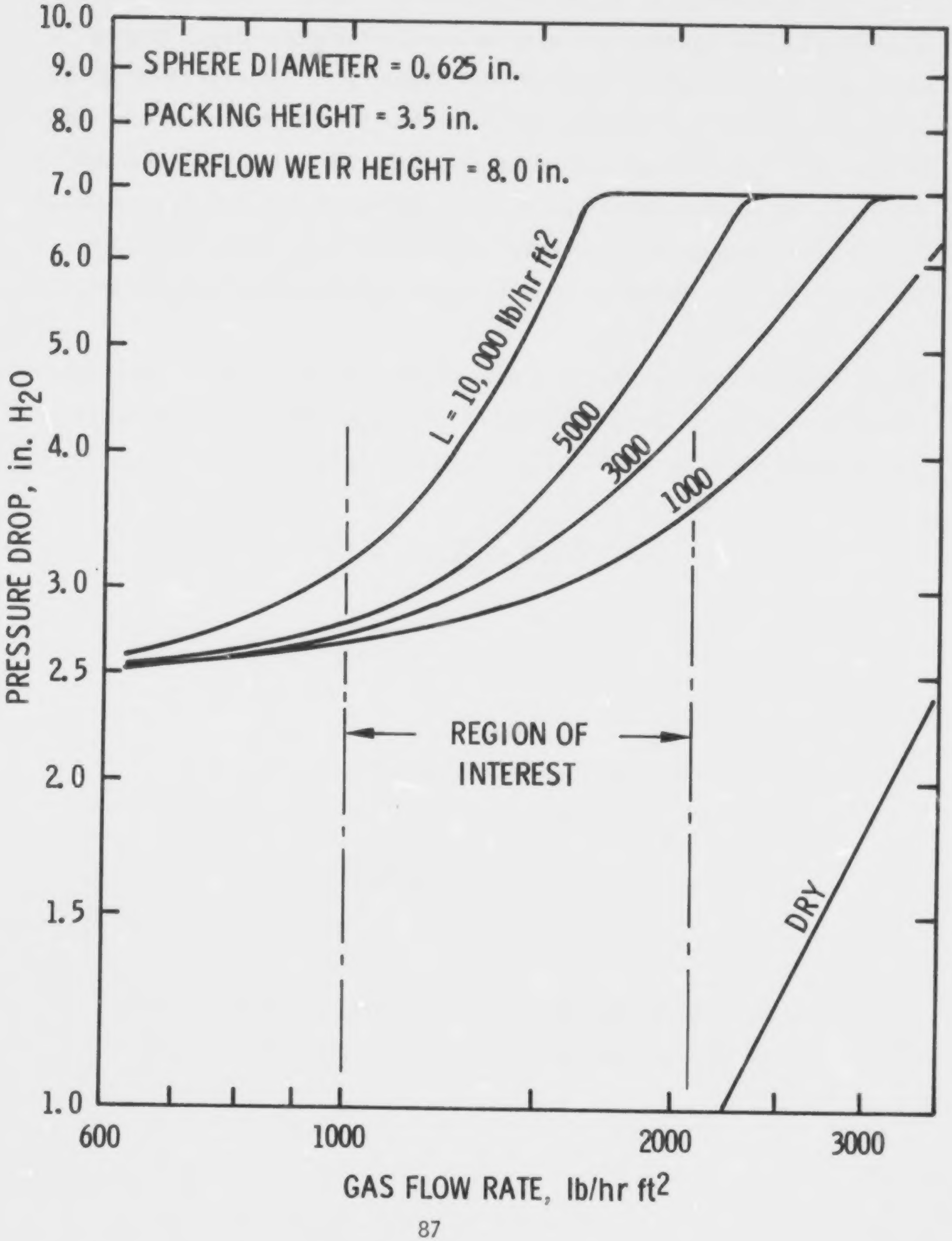


FIGURE 19
PREDICTED PRESSURE DROP THROUGH GLASS-SPHERE REGION AND TURBULENT LAYER OF HYDRO-FILTER



PARTICULATE REMOVAL

Particulate removal in the Hydro-Filter scrubber is obtained within the bed of glass spheres and also within the turbulent-layer region directly above the glass spheres (see Figure 17). Calvert (Ref. 2 and 42) has found particulate removal in packed beds to be consistent with an inertial impaction collection mechanism. He has also presented (Ref. 43) an equation based on this mechanism for particulate removal in a frothing bed on a sieve tray. Similarly, Pozin et al. (Ref. 44) have also found removal in froth to follow an impaction mechanism.

In accordance with the theories presented in Refs. 2 and 43, particulate removal within the glass-sphere and turbulent-layer regions of the Hydro-Filter for particles of size i can be represented by:

$$\eta_M(i) = 1 - \exp\left[-\beta_1 (L/G) K_i H_M / d_M\right] \qquad (52)^{*}$$

$$\eta_T(i) = 1 - \exp\left[-\beta_2 F^2 K_i H_T / d_M\right] \qquad (53)^{**}$$

The inertial impaction parameter is defined as:

$$K_i = 1.29 \times 10^{-10} \frac{G \rho_p d_i^2}{9 \rho_G \epsilon \mu_G d_M} \qquad (54)$$

---

* The term L/G was not included in the original theory.

** The term $\frac{H_T}{d_M}$ was not included in the original theory.

The height of the turbulent layer is estimated from a correlation presented by Lowry and Van Winkle (Ref. 45):

$$H_T = 1.1 + 7.5 \times 10^{-7} \left(\frac{G}{\rho_G}\right)^2 \left(\frac{\rho_G}{\rho_L - \rho_G}\right) \qquad (55)$$

with the following constraint:

$$H_T \geq H_W - H_M \qquad (56)^*$$

The total removal of particulates of size i within each stage** (glass-sphere and turbulent layer region) of a Hydro-Filter is given by:

$$\eta(i) = 1 - [1 - \eta_M(i)][1 - \eta_T(i)] \qquad (57)$$

The numerical constants β_1, and β_2 in Eqs. 52 and 53 were obtained by fitting the overall particulate removal (Eq. 8) to vendor test data (Ref. 41), using the assumed flyash distribution curve shown in Figure 2. The comparison between predicted and measured overall removals for values of β_1, and β_2 of 0.2 and 6.3, respectively, are shown in Figure 20. In Figure 21, predicted overall particulate removal efficiency is shown as a function of gas rate and liquid-to-gas ratio, based on the fitted coefficients and the assumed distribution curve (Figure 2).

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* The overflow weir height is measured from the base of the glass spheres.

** The Hydro-Filter is normally operated in either a single-stage (one marble-bed) or double-stage (two marble-beds) configuration. For a double-stage configuration, the particulate removal is given by:

$$\eta_i(2\text{-stage}) = 1 - [1 - \eta_i(1^{st}\text{stage})][1 - \eta_i(2^{nd}\text{stage})]$$

FIGURE 20
COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF OVERALL PARTICULATE REMOVAL FOR HYDRO-FILTER

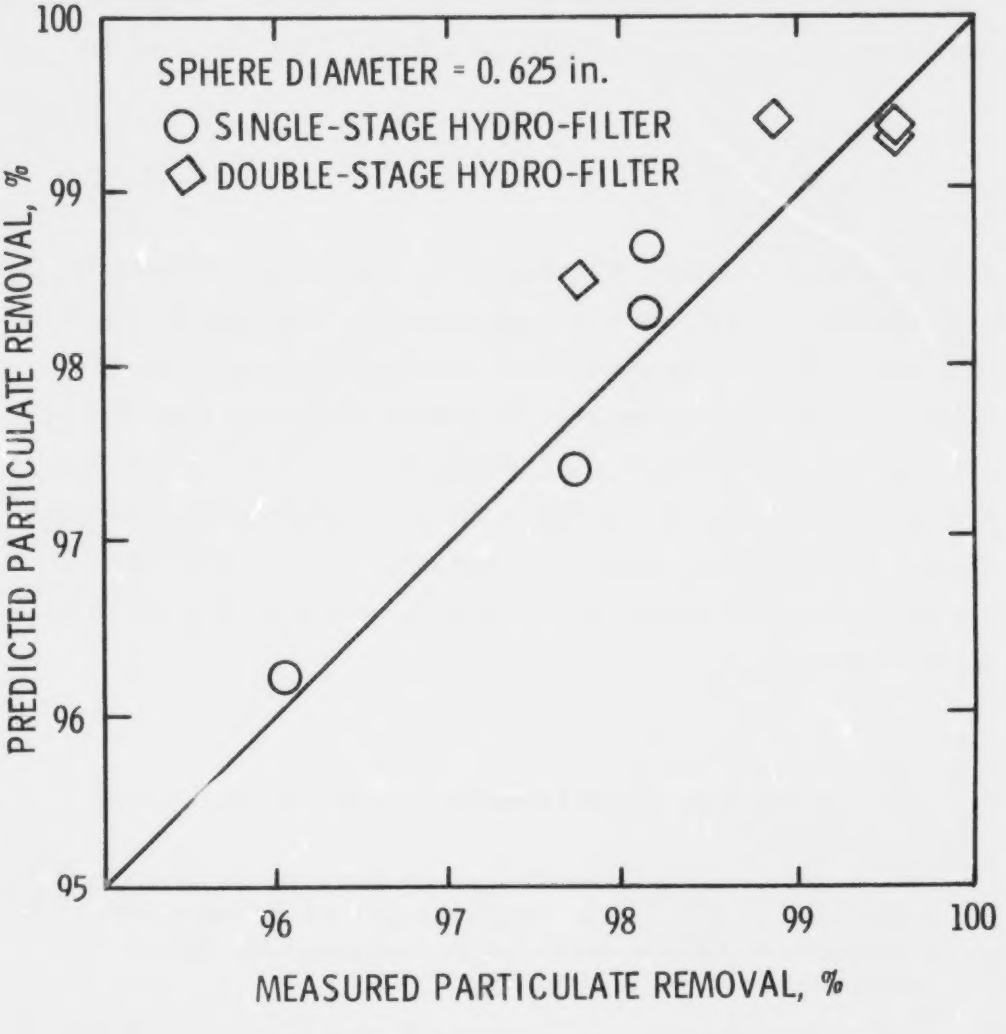
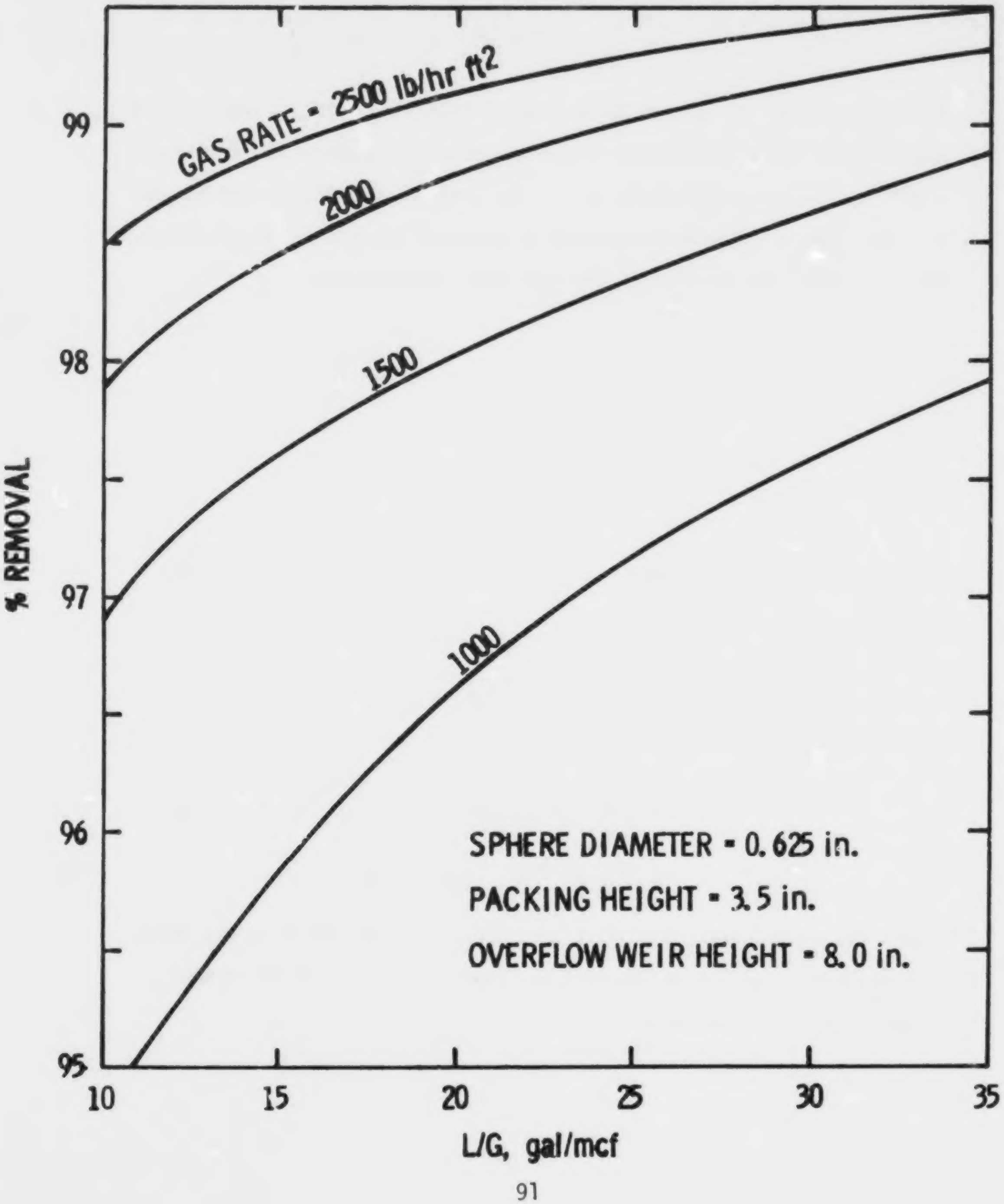


FIGURE 21

PREDICTED OVERALL PARTICULATE REMOVAL EFFICIENCY FOR SINGLE-STAGE HYDRO-FILTER



For the fitted values of the coefficients β_1, and β_2, Eq. 57 becomes:

$$\eta(i) = 1 - \exp\left[-0.2(L/G) K_i H_M/d_M - 6.3 F^2 K_i H_T/d_M\right] \quad (58)$$

As an example, for a gas flow rate of 2000 lb/hr ft^2, a liquor flow rate of 3000 lb/hr ft^2 (L/G = 12.7 gal/mcf), a sphere diameter of 0.625 in., a packing height of 3.5 in. and an overflow weir height of 8 in., the particulate removal efficiency from Eq. 58 is as follows for various characteristic particle diameters:

d_i, microns	% Removal
1	15
2	48
5	98
10	100

The predicted overall removal efficiency (see Figure 21) for the above example is 98.2%.

The form of the expression for particulate removal which will be tested with the data obtained at the facility is:

$$\eta(i) = 1 - \exp\left[-\beta_1 (L/G)^{\beta_2} K_i H_M/d_M - \beta_3 F^2 K_i H_T/d_M\right] \quad (59)$$

where the constants β_1, β_2, and β_3 are to be fitted to the data. The parameters F and H_T will be directly measured from photographic data, if possible.

ABSORPTION OF SO_2

The major assumptions made in the formulation of the mathematical model for mass transfer of SO_2 are:

1. (1) Plug flow of gas phase
2. (2) Completely back-mixed bulk liquid phase throughout entire mass transfer region of Hydro-Filter, i.e. uniform composition (and temperature) within bulk liquid phase. Furthermore, the liquid "film" between vapor and bulk liquid is also assumed to be at a uniform composition (and temperature).
3. (3) Liquor is at all times in equilibrium with an interfacial CO_2 vapor pressure of 0.1 atm of CO_2, i.e. rate of CO_2 absorption (and desorption) is very large.

The development of the equations for describing SO_2 mass transfer in the glass-sphere and turbulent layer regions of the Hydro-Filter will not be presented here, due to the length of the venturi presentation. The basic differential equations describing SO_2 mass transfer, heat transfer and solid dissolution are similar to those presented for the venturi.

As an example of a result of the Hydro-Filter modeling, for the interfacial SO_2 mole fraction, y^*, equal to zero (gas phase controlling), SO_2 removal becomes:

$$SO_2 \text{ Removal} = 1 - \exp\left[- \frac{(k_G a)_M H_M}{G} - \frac{(k_G a)_T H_T}{G} \right] \qquad (60)$$

where

$$(k_G a)_M = \beta_1 \, G_L^{0.2} \left[\frac{d_M G}{\mu (1-\epsilon)} \right]^{-0.35} \frac{6(1-\epsilon)}{d_M} \qquad (61)$$

and

$$(k_G a)_T = \beta_2 \sqrt{\frac{\mathcal{D} G \rho_G (1-F)}{H_T \, d_M^2}} \qquad (62)$$

The coefficients β_1, and β_2 are to be fitted to the data obtained at the test facility for Na_2CO_3 aqueous scrubbing of mixtures of air and SO_2 (see Ref. 55)*.

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* Figure 22 (which showed "Predicted Mass-Transfer-Limited SO_2 Removal") has been omitted in this 2nd edition of the paper since discussions with the vendor have indicated that the figure was probably in error. Figure 22 was to have appeared on page 50.

FIGURE 22

Not included in this revision

TCA SCRUBBER

A two-stage TCA scrubber, shown schematically in Figure 23, utilizes a packing of low density plastic spheres which are free to move between retaining grids. Normal operation is as follows (Ref. 46): Gas enters the scrubber at the bottom and passes upward through the packing, while the liquor stream is sprayed downward from the top. The countercurrent flow forces the spheres upward in a random, turbulent pattern and the degree of bed agitation can be changed by controlling the liquid and gas rates.

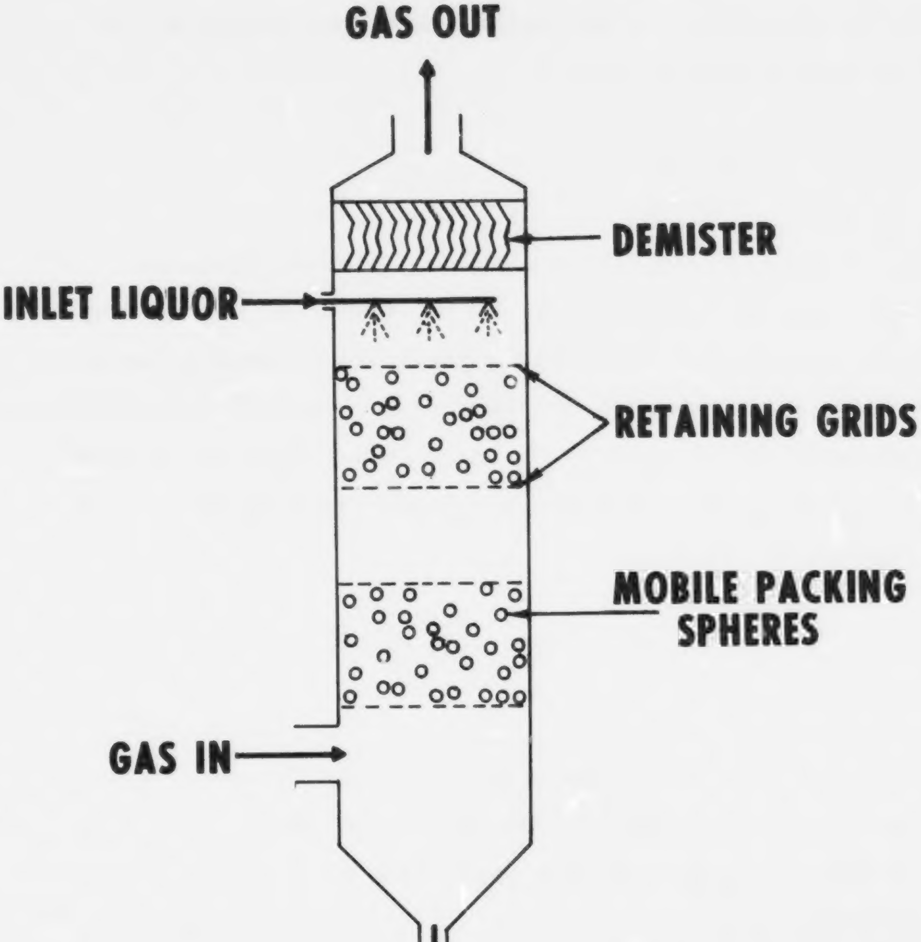
PRESSURE DROP

Curves showing total pressure drop (include demister) for 1, 2 and 3-stage TCA pilot scrubbers have been furnished by UOP (Ref. 47). Thefollowing equations were fit (multiple regression computer program) to the pressure drop curves, under the assumption that the form of the correlation for pressure drop in the packing section is the same as that given by Leva (Ref. 36).

$$(\Delta p)_P = 1.52 \times 10^{-8} \frac{m H_P G^2}{d_P} \exp\left[8 \times 10^{-3} (L/G)^{0.9} G^{0.17}\right] \qquad (63)$$

$$(\Delta p)_D = 1.35 \times 10^{-7} G^2 \qquad (64)$$

FIGURE 23
SCHEMATIC OF TWO-STAGE TCA SCRUBBER WITHOUT TRAP-OUT TRAY



A comparison between predicted and measured (Ref. 48) pressure drops for a two-stage TCA is shown in Figure 24.

In Figure 25 the predicted total pressure drop is shown for a 2-stage TCA scrubber and demister, as a function of gas and liquid flow rates. Typically, the pressure drop through the demister section is less than 15% the total pressure drop.

PARTICULATE REMOVAL

Particulate removal in the TCA scrubber is obtained within the fluidized-bed stages. Calvert (Ref. 42) has found that inertial impaction is the predominant mechanism for particle collection in packed-beds. With the assumption that the form of the expression for particulate removal in a TCA stage is the same as that for a packed-bed stage, the following equation is proposed for estimating removal in a TCA stage:

$$\eta(i) = 1 - \exp\left[-\psi(L/G, G)\, K_i\, m\, H_p/d_p\right] \qquad (65)$$

The inertial impaction parameter is defined in Eq. 6, and overall removal is obtained from Eq. 8. The function of $\psi(L/G, G)$ was determined by using a multiple regression fit of Eq. 65 to overall particulate removal data from Ref. 49, for a 2-stage TCA scrubber. The resultant form of Eq. 65 is:

$$\eta(i) = 1 - \exp\left[-5\times10^{-17}(L/G)^{3.3}\, G^{3.66}\, K_i\, m\, H_p/d_p\right] \qquad (66)$$

FIGURE 24

COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF PRESSURE DROP FOR TWO-STAGE TCA

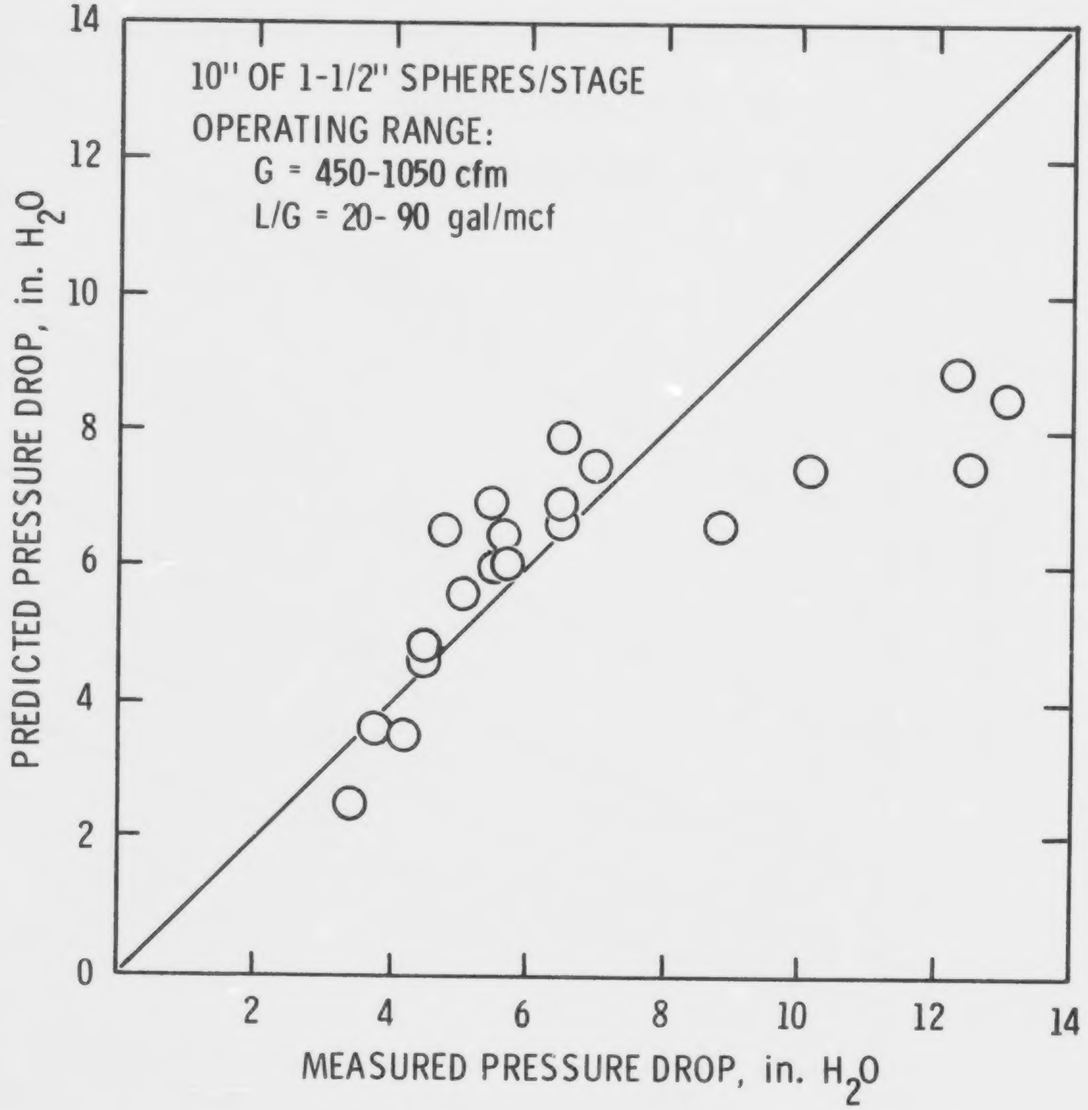
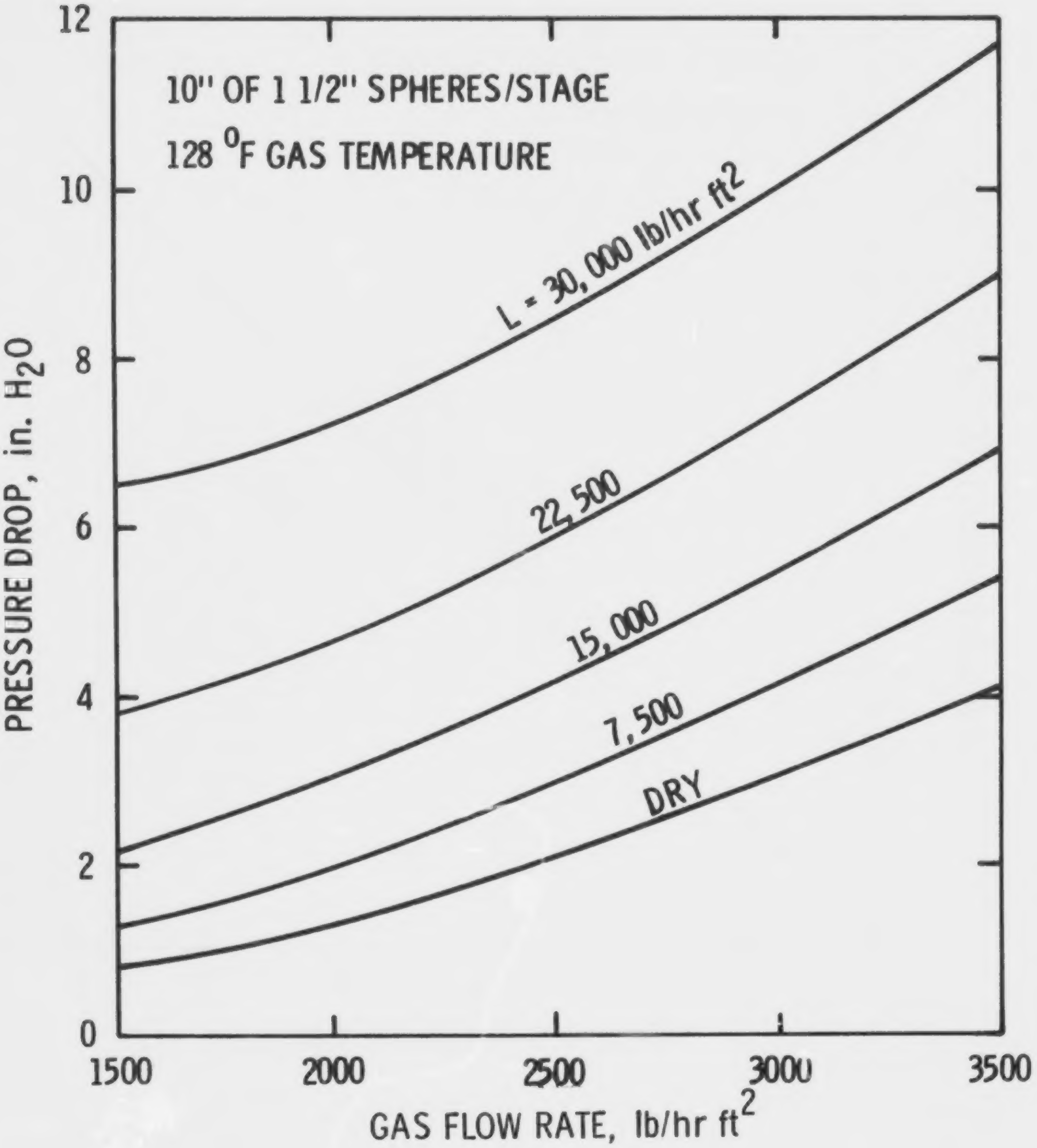


FIGURE 25
PREDICTED PRESSURE DROP THROUGH TWO-STAGE TCA SCRUBBER



A comparison between the predicted (Eqs. 66 and 8) and measured (Ref. 49) overall removals is shown in Figure 26, using the flyash size distribution given in Ref. 48. In Figure 27, the predicted overall particulate removal efficiency for a 2-stage TCA is shown as a function of gas and liquid flow rates, using the assumed Shawnee flyash distribution (Figure 2).

The form of the expression for particulate removal which will be tested with the data obtained at the test facility is:

$$\eta(i) = 1 - \exp\left[-\beta_1 (L/G)^{\beta_2} K_i\, m\, H_p/d_p\right]$$

where the constants β_1, and β_2 are to be fitted to the data.

ABSORPTION OF SO_2

The major assumptions made in the formulation of the mathematical model for absorption of SO_2 are:

(1) Plug flow of gas phase.

(2) A dispersion model can be used to describe axial mixing within the liquid phase. This dispersion model considers all deviations from plug flow to be centered in a term analogous to Fick's law of diffusion.

(3) Liquor is at all times in equilibrium with an interfacial CO_2 vapor pressure of 0.1 atm of CO_2, i.e. rate of CO_2 absorption (and desorption) is large.

FIGURE 26
COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES OF OVERALL PARTICULATE REMOVAL FOR TWO-STAGE TCA

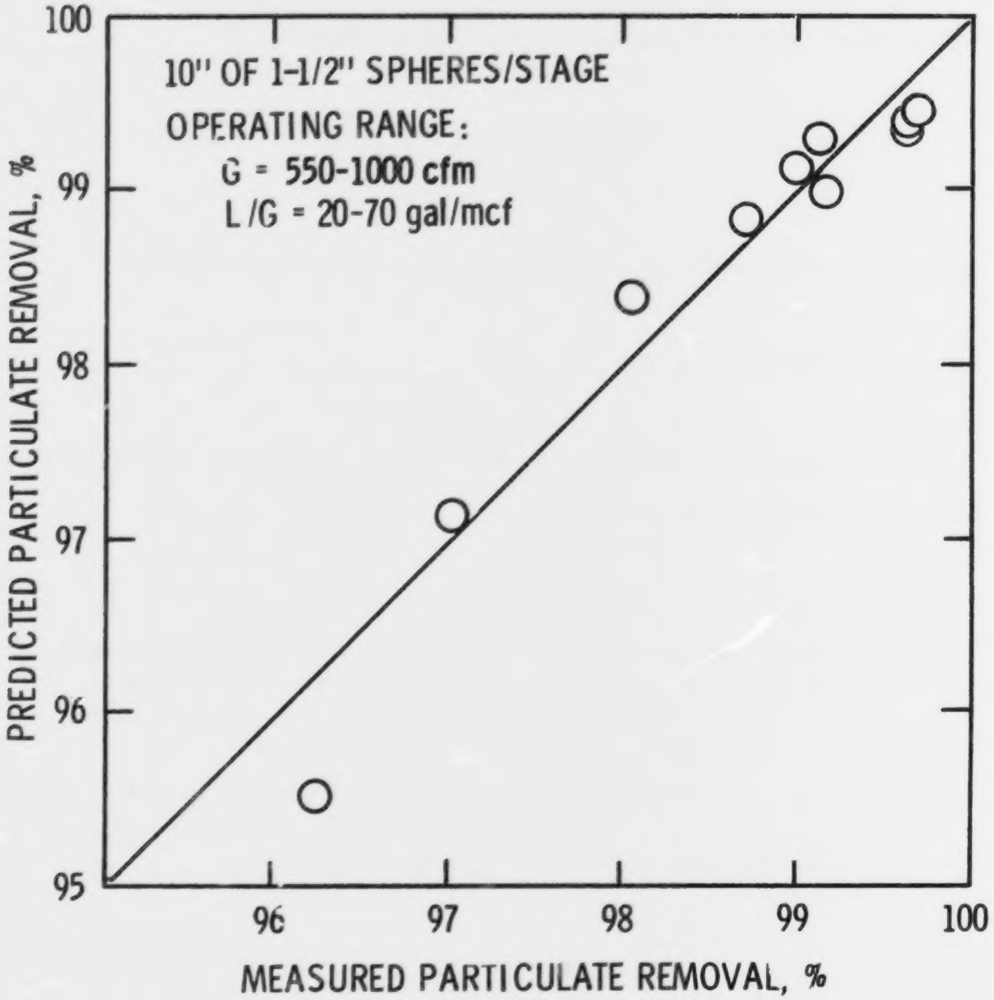
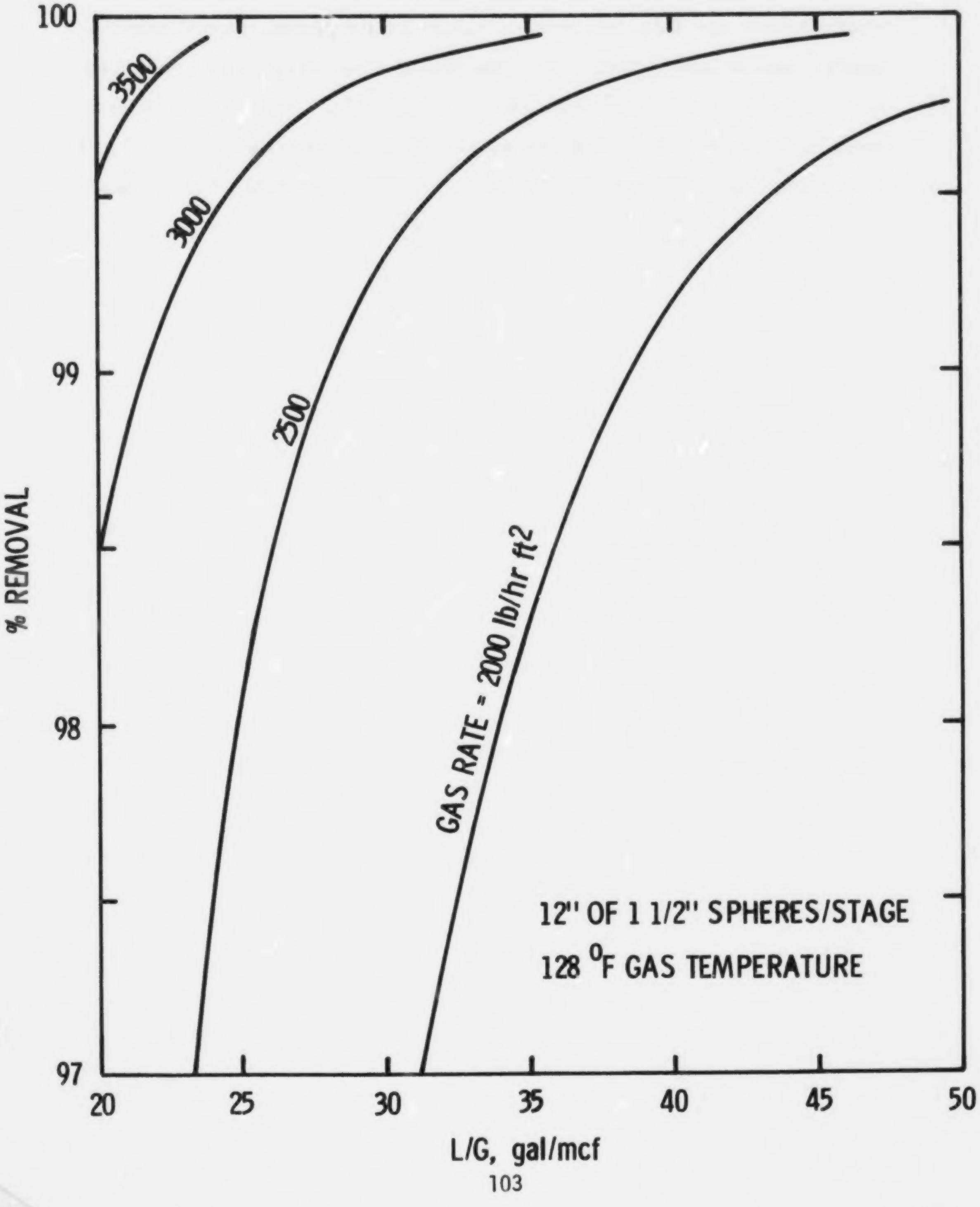


FIGURE 27
PREDICTED OVERALL PARTICULATE REMOVAL EFFICIENCY FOR TWO-STAGE TCA



As with the Hydro-Filter, the development of the equations for describing SO_2 absorption in the TCA will not be presented here.

Correlations for axial dispersion in the liquid phase, liquid holdup, mass transfer coefficient and interfacial area have been presented by Khanna (Ref. 50) and Chen (Refs. 51 and 52). The partial differential equations describing the mass transfer between liquid and gas have been discussed by Khanna (Ref. 50) and Miyauchi (Ref. 53 and 54).

NOMENCLATURE

a	gas-liquid interfacial area per scrubber volume, 1/ft
A	cross-sectional area, ft^2
C_D	drag coefficient
C_f'	characteristic factor of packing, ft^{-1}
C_p	specific heat, BTU/lb^{o}R
d_i	diameter of particulate of size i , micron
d_M	diameter of glass spheres, ft
d_r	diameter of plastic spheres, ft
D_o	mean diameter of droplets, micron
$\mathcal{D}$	diffusivity of SO$_2$ in flue gas, lb^2/hr
E_i	collection efficiency for particulate of size i
F	specific gravity of turbulent layer
g_c'	gravitational acceleration, lb$_m$ ft/lb$_f$ hr^2
G	gas flow rate, lb/hr ft^2
h_G	gas-side heat transfer coefficient, BTU/ft^2 hr^{o}R
h_L	liquid-side heat transfer coefficient, BTU/ft^2 hr^{o}R
H_M	height of glass-sphere region, ft

H_P	static height of packing for a single-stage TCA, ft
H_T	height of turbulent layer, ft
H_W	height of overflow-weir, ft
k_G	gas-side mass transfer coefficient, lb mol/hr ft^2
k_L	liquid-side mass transfer coefficient, ft/hr
k_L^o	liquid-side mass transfer coefficient in absence of chemical reaction, ft/hr
k_s	reaction rate constant based upon unit surface, ft/hr
K	inertial impaction parameter
K_G	overall gas-phase mass transfer coefficient, lb mol/hr ft^2
K_{WG}	overall gas-side mass transfer coefficient for diffusion of water vapor, lb mol/hr ft^2
L/G	liquid-to-gas ratio, gal/mc f
m	Henry's law constant, ft^3/ lb mol
n	number of stages in TCA
N	total number of solid spheres per unit volume of liquid, $1/ft^3$
Δp	pressure drop, in-H_2O
Q_G	volumetric flow rate of gas, cfs
Q_L	volumetric flow rate of liquid, gpm
r	radius of solid particle, ft
R	initial radius of solid particle, ft

Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	time, hr
T	temperature, °F
T^*	temperature of gas-liquid interface, °F
U	gas velocity, ft/sec
v	liquid droplet velocity, ft/sec
W_i	weight fraction of particulate of size i
X_A	concentration of dissolved A (SO_2) at gas-liquid interface, lb mol/ft^3
X_B	initial concentration of dissolved reagent B, lb mol/ft^3
X_{CA}	concentration of total calcium in solution, lb mol/ft^3
X_{CA}^*	concentration of total calcium in solution in equilibrium with liquid and solid phases, lb mol/ft^3
$X_{H_2SO_3}$	concentration of H_2SO_3 (or molecular SO_2) in bulk liquid, lb mol/ft^3
$\bar{X}_L$	concentration of all species in solution, lb mol/ft^3
X_{MG}	concentration of magnesium in solution, lb mol/ft^3
X_S	concentration of solid species in slurry, lb mol/ft^3
X_{SO_3}	concentration of SO_3 species in solution, lb mol/ft^3
X_{SO_4}	concentration of SO_4 species in solution, lb mol/ft^3

y	mole fraction of SO_2 in gas phase
y^*	mole fraction of SO_2 in gas phase in equilibrium with concentration of SO_2 (H_2SO_3) in bulk phase of liquid
Y	mole fraction of water vapor in gas phase
Y^*	mole fraction of water vapor at gas-liquid interface
z	distance, ft
Z	distance from point of droplet formation, ft
ΔZ	height of differential element, ft

Greek Letters

α_0 α_1	constants in Eq.
$\beta_1 \rightarrow \beta_6$	constants to be determined from data
γ_s	specific surface area, ft^2/lb
ϵ	void fraction, i.e. fraction of scrubber volume occupied by gas
η	particulate removal efficiency
λ	constant in Eq. 26
λ'	heat of vaporization of H_2O, BTU/lb mol
μ	viscosity, lb/ft sec
ν	stoichiometric coefficient relating the number of moles of B reacting with one mole of A
ρ	density, lb/ft^3
σ	surface tension, lb/sec^2
Φ, Φ'	equilibrium functions (Radian Computer Program)
ψ	function

Subscripts

D	refers to demister
G	refers to gas
i	refers to particulate of size i
L	refers to liquid
M	refers to glass-sphere region or glass spheres
o	refers to point of droplet formation or point at $z = 0$
p	refers to solid particulates
P	refers to plastic sphere packing in TCA
s	refers to solids
t	refers to venturi throat
T	refers to turbulent layer region

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A MODEL FOR THE LIMESTONE INJECTION - WET SCRUBBING PROCESS FOR SULFUR DIOXIDE REMOVAL FROM POWER PLANT FLUE GAS

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1.0 INTRODUCTION

The growing problem of atmospheric pollution by sulfur oxides has promoted a large amount of research and development on removal process for power plant flue gases. Of the several processes that have been proposed, use of lime or limestone in a wet scrubber is one of the more promising.

The limestone injection - wet scrubbing (LIWS) process involves injecting limestone into the power plant boiler and catching it in a wet scrubber after the air heater (see Figure 1). Proponents of the process claim that injection of limestone into the boiler removes a portion of the sulfur dioxide ahead of the scrubber, provides protection from corrosion by sulfur trioxide and alkali salts, and converts the limestone to quicklime, a more reactive form for use in the scrubber (TE-001, PL-002, MA-014). The limestone tail-end addition (LTEA) process involves adding the limestone in the slurry handling system. In Figure 1, the recycle hold tank would be one possible addition point. The LTEA process avoids the injection of limestone into the boiler. The major components of the LIWS and LTEA processes are the scrubber and the liquid slurry handling system. The LIWS and LTEA processes are termed "throwaway processes" in that the by-product sludge containing primarily fly ash, calcium sulfite and calcium sulfate is currently considered a waste stream.

A number of similar wet scrubbing processes are being considered for the control of SO_2 emissions from stationary sources (MA-038, GR-009, DE-036, SL-004, TE-001, CL-005, BA-019, HA-027, BR-014, CH-029, CH-030, SH-031). These include the use of limestone, lime, and magnesia addition into the control process liquor. A useful chemical by-product is to be recovered from several of these processing schemes.

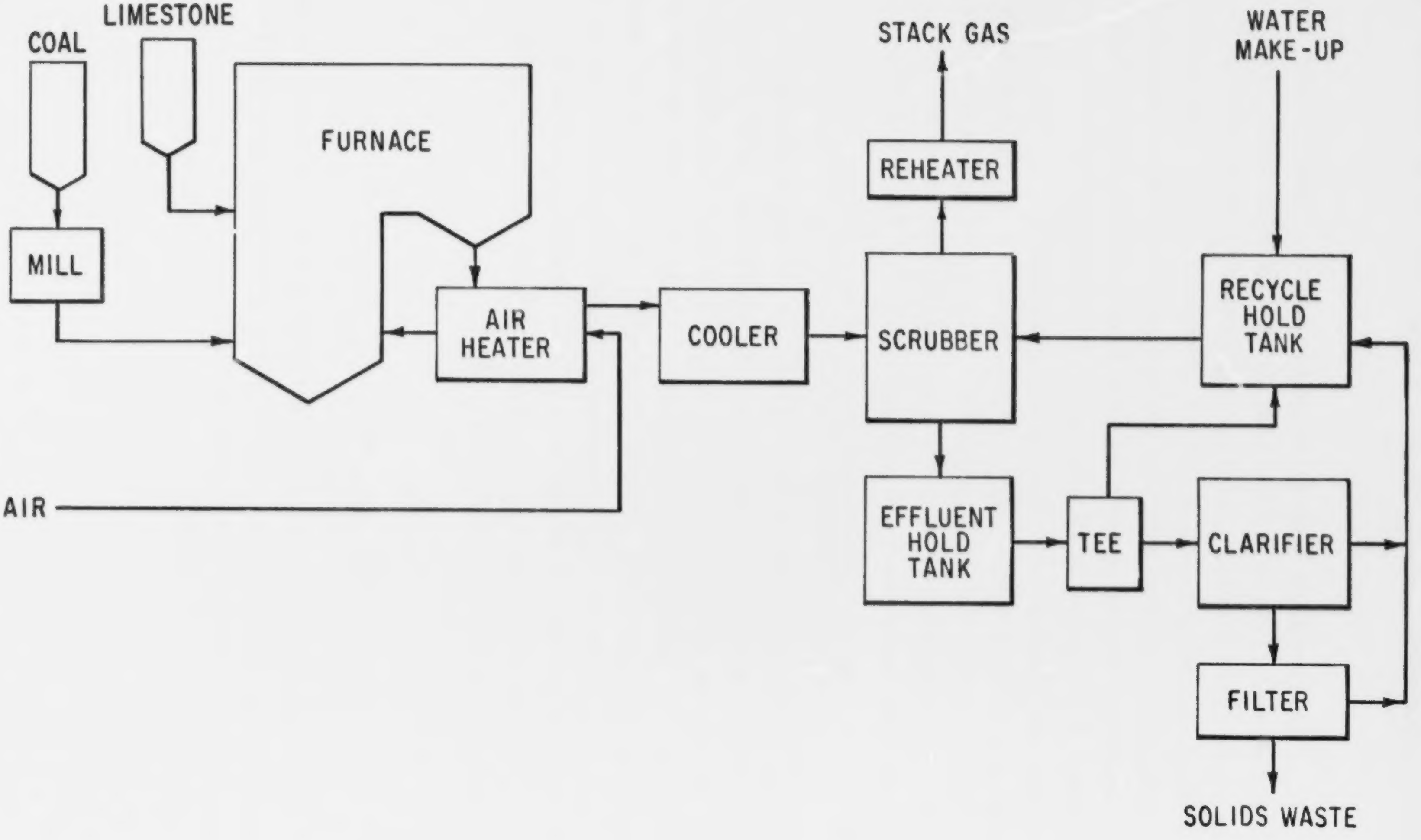

FIGURE 1 - SCHEMATIC OF LIMESTONE INJECTION-WET SCRUBBING PROCESS

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Although a number of pilot unit programs have been conducted and several commercial installations have been operating periodically, processing problems such as scaling and low SO_2 removal still remain unsolved. This, of course, is evidence that the process design of these wet scrubbing processes is not as simple as was first anticipated. Radian's approach to process engineering lime/limestone wet scrubbing systems has been to develop an understanding of their process chemistry. This technology then provides a sound basis for (1) determining the technical feasibility of process alternatives, (2) estimating process flow rates and compositions, (3) correlating experimental data, and (4) defining major process variables.

The purpose of this paper is to describe Radian's development of a lime/limestone wet scrubbing process model and to report some of the simulation results from a parameter study of the LIWS prototype system. A comparison of the LIWS and LTEA processes is made by comparing the results of several simulation cases of each process. Details of the process model will be described in terms of the LIWS prototype system. However, the model is easily adapted to other wet scrubbing schemes employing the same chemical species.

2.0 PROCESS DESCRIPTION

Numerous processing schemes are possible for LIWS and LTEA processes. One of the more promising wet scrubbing schemes for the LIWS is shown in Figure 2.

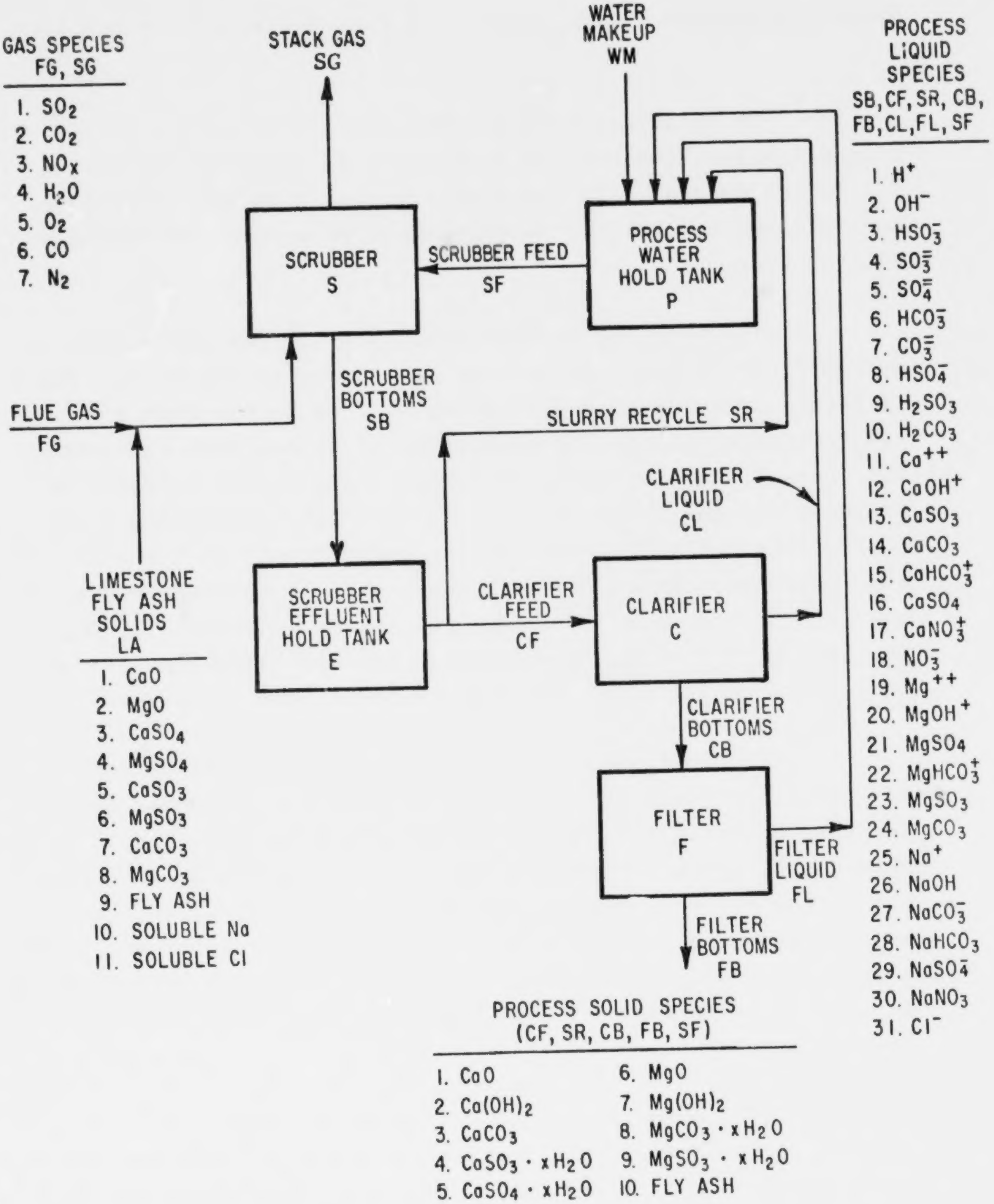

FIGURE 2 - WET SCRUBBING SCHEME

In this flow arrangement, the slurry recirculation system involves two holding tanks plus a clarifier and filter for solids removal. In the LIWS process, flue gas containing both fly ash and boiler-reacted limestone enters the bottom of the scrubber.

The chemical constituents entering the wet scrubbing system from the gas-solid stream are listed on Figure 2. The limestone injected into the boiler will be in the form of (1) the oxide (calcium or magnesium) if it has been calcined, (2) the sulfate or sulfite if it has reacted with sulfates or sulfites via gas-solid reaction in the high temperature zone of the flue gas train, and (3) the carbonate if it has not reacted or has recombined with CO_2 in the lower temperature zone of the flue gas. The flue gas stream contains SO_2, CO_2, NO_x, and O_2 which may be absorbed. Soluble sodium, potassium, and chlorides can enter the aqueous phase from the fly ash.

In the scrubber, the flue gas (FG) and limestone-fly ash solids (LA) are contacted with a basic scrubber liquor. The scrubber feed (SF) stream can be either a clear liquid or a slurry. Due to the chemical species entering the aqueous phase and to the various chemical reactions occurring within the aqueous phase, a number of ionic and nonionic species are present in the process liquid stream. The list of process liquid species is also given in Figure 2. A list of the possible process solid species is also shown.

If a clear liquid SF stream is utilized (no slurry recycle), the SF flow rate must be large enough that the liquid phase contains sufficient basic species to neutralize the SO_2 and CO_2 absorbed in the scrubber. If a slurry SF stream is utilized, additional basic species in the solid-phase will be available for reaction in the scrubber and the SF flow rate required to remove a given amount of SO_2 will be less than with a clear liquid feed.

The chemical objective of the LIWS process is to promote the overall reaction of gaseous SO_2 reacting with solid calcium or magnesium oxides to give solid sulfites, i.e.,

$$SO_2(g) + MeO(s) + H_2O(aq) \rightarrow MeSO_3 \cdot xH_2O + H_2O(aq).$$

Gaseous CO_2 will react in a similar fashion to form solid carbonates. Oxidation of the sulfite will give rise to sulfates in the system.

The actual reaction path involves a number of serial steps. The gaseous species SO_2, CO_2, NO_x, and O_2 must be absorbed by the liquid at the gas-liquid interface (see Figure 3). Water is simultaneously being transferred in the opposite direction due to its vaporization occurring in the scrubber. The driving force for the sorption of the acidic gas species is maintained by the presence of sufficient basic species in the liquid phase. In the scrubber, this basicity can be furnished by the dissolution of solids such as calcium hydroxide, calcium carbonate, magnesium hydroxide, and magnesium carbonate. In the LIWS process, the calcium and magnesium oxides most probably hydrate to form the solid hydroxides, which then dissolve to provide calcium, magnesium, and hydroxyl ions.

The LIWS system involves a three-phase reaction system which could be controlled by one or more individual steps. The resistances to mass transfer are represented by both sides of the vapor-liquid film, liquid-phase reactions, liquid-solid films, diffusion through solid layers, and reactions with solids. The oxidation of sulfites to sulfates will influence both vapor-liquid and solid-liquid equilibria.

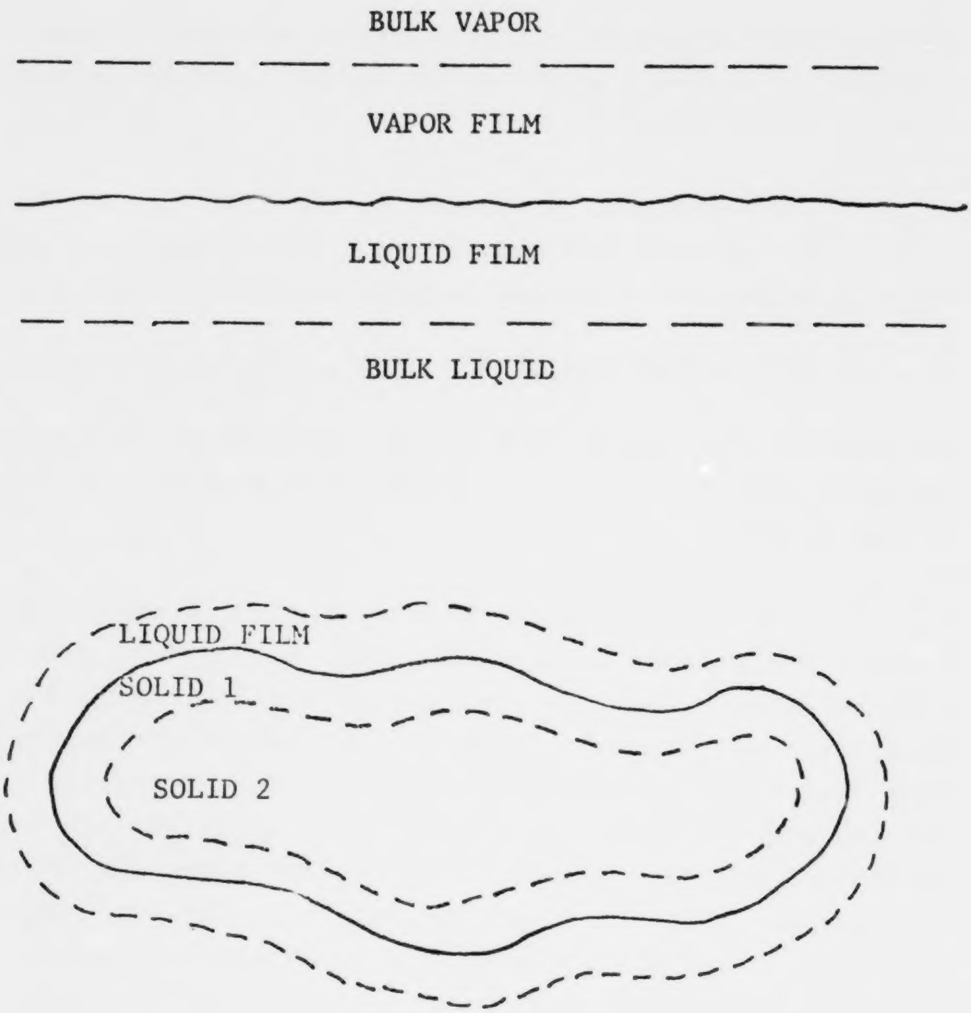

FIGURE 3 - THREE PHASE SYSTEM

The hydration of the calcium and magnesium oxides may take place in any part of the wet scrubbing network. The dissolution of the hydroxides and carbonates depends upon the chemical environment in a particular scrubbing vessel. That is to say, the driving force for dissolution will be largest in the scrubber where it is most acidic. The driving force for dissolution in the holding tanks and clarifier where it is more basic will be small. In fact, if the holding times are sufficiently large, solid-liquid equilibrium with respect to dissolution of these species will be closely approached.

The liquor in the scrubber will become supersaturated with respect to calcium sulfite and calcium sulfate. The degree of supersaturation occurring in the scrubber will depend upon the liquid residence time and the rates of (1) sulfur dioxide absorption, (2) sulfite oxidation, (3) calcium hydroxide and carbonate dissolution, and (4) calcium sulfite and sulfate precipitation. The rate of calcium sulfite and sulfate precipitation is in turn dependent upon the degree of supersaturation. Precipitation of calcium sulfite and sulfate on scrubber components has been a major operating problem for the LIWS process.

Thus, it is apparent that proper design of the LIWS system should promote the vapor-liquid mass transfer of SO_2 absorption and the solid-liquid mass transfer of calcium hydroxide and carbonate dissolution in the scrubber. The precipitation of calcium sulfite and sulfate should be discouraged in the scrubber and encouraged in the ancillary slurry handling system. The slurry handling system should be designed to provide (1) a basic scrubber feed stream and (2) method for removing the waste solids without undue loss of reactive lime or limestone.

3.0 PROCESS MODEL

Based upon the present knowledge of the process chemistry and equipment operating characteristics, Radian has formulated a LIWS process model using appropriate material balance considerations and processing assumptions. Due to the absence of rate data for this process, Radian formulated the model based upon conversions for these rate steps as specified by model inputs or by equilibrium assumptions.

The present Radian model is a series of computer routines which consists of three major elements: (1) equipment subroutines that model each process unit, (2) convergence subroutines that force convergence of the model's iterative parameters, and (3) an executive system that interconnects the processing units in the appropriate fashion and controls the sequencing of computer operations.

3.1 Process Chemistry

The heart of the process model is its ability to describe the process chemistry adequately. Thus, Radian started this program by developing a chemical equilibrium program for the vapor-liquid-solid system encountered in the LIWS process. Vapor-liquid and liquid-solid mass transfer rates are usually calculated using a driving force term that is a measure of the distance from equilibrium. For some pieces of equipment the assumption of various streams being in equilibrium is reasonable. Hence the ability to predict equilibrium for the vapor-liquid-solid system is a prerequisite for process modeling, data analysis, and process engineering calculations.

The development of the equilibrium program began with an investigation of the literature to determine the significant chemical species, reactions, and equilibrium constants.

The chemical species in the aqueous phase originate from lime (CaO, MgO), flue gas (CO_2, SO_2, SO_3, O_2, NO_x), and fly ash (Na, K, Cl, plus others). A list of neutral and ionic species formed by these species upon interaction with water was screened to retain only the species having non-negligible influences. Some species were treated in a simplified manner so as to increase computational efficiency. The potassium species have been treated as "effective" sodium since the equilibrium behavior of the two is similar. Also, the nitrogen oxides have been treated as forming only nitrates in solution.

A chemical equilibrium program was formulated based upon the specification of nine key species in the limestone wet scrubbing process (CaO, MgO, Na_2O, SO_2, SO_3, CO_2, N_2O_5, HCl, and H_2O). Sulfite oxidation is considered to be a rate controlled step in the limestone wet scrubbing process so that both the amounts of sulfite and sulfate sulfur are specified as key species. The anhydride of nitric acid, N_2O_5, is specified for the NO_x contribution to the liquid phase.

The chemical reactions considered in the equilibrium formulation are listed in Table I. There are twenty-two dissociation-type equations, seven solubility product relations, and two gas solubility equations. These equilibrium relationships were expressed as activities using molality times an activity coefficient. These equations were combined with mass balance equations. The set of nonlinear equations was solved in the log molality domain.

TABLE I - REACTIONS CONSIDERED

LIQUID PHASE REACTIONS:

1) $H_2O \rightleftarrows H^+ + OH^-$

2) $HSO_3^- \rightleftarrows H^+ + SO_3^=$

3) $H_2SO_3 \rightleftarrows H^+ + HSO_3^-$

4) $HSO_4^- \rightleftarrows H^+ + SO_4^=$

5) $HCO_3^- \rightleftarrows H^+ + CO_3^=$

6) $H_2CO_3 \rightleftarrows H^+ + HCO_3^-$

7) $CaOH^+ \rightleftarrows Ca^{++} + OH^-$

8) $CaSO_3 \rightleftarrows Ca^{++} + SO_3^=$

9) $CaSO_4 \rightleftarrows Ca^{++} + SO_4^=$

10) $CaCO_3 \rightleftarrows Ca^{++} + CO_3^=$

11) $CaHCO_3^+ \rightleftarrows Ca^{++} + HCO_3^-$

12) $CaNO_3^+ \rightleftarrows Ca$

13) $MgOH^+ \rightleftarrows Mg^{++} + OH^-$

14) $MgSO_3 \rightleftarrows Mg^{++} + SO_3^=$

15) $MgSO_4 \rightleftarrows Mg^{++} + SO_4^=$

16) $MgCO_3 \rightleftarrows Mg^{++} + CO_3^=$

17) $MgHCO_3^+ \rightleftarrows Mg^{++} + HCO_3^-$

18) $NaOH \rightleftarrows Na^+ + OH^-$

19) $NaSO_4^- \rightleftarrows Na^+ + SO_4^=$

20) $NaCO_3^- \rightleftarrows Na^+ + CO_3^=$

21) $NaHCO_3 \rightleftarrows Na^+ + HCO_3^-$

22) $NaNO_3 \rightleftarrows Na^+ + NO_3^-$

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TABLE I - REACTIONS CONSIDERED (Cont'd.)

LIQUID-SOLID EQUILIBRIA:

23) $CaCO_3(S) \rightleftarrows Ca^{++} + CO_3^{=}$

24) $CaSO_4(S) \rightleftarrows Ca^{++} + SO_4^{=}$

25) $CaSO_3(S) \rightleftarrows Ca^{++} + SO_3^{=}$

26) $Ca(OH)_2(S) \rightleftarrows Ca^{++} + 2OH^{-}$

27) $Mg(OH)_2(S) \rightleftarrows Mg^{++} + 2OH^{-}$

28) $MgCO_3(S) \rightleftarrows Mg^{++} + CO_3^{=}$
29) $MgSO_3(S) \rightleftarrows Mg^{++} + SO_3^{=}$

GAS-LIQUID EQUILIBRIA

30) $SO_2(g) + H_2O \rightleftarrows H_2SO_3$

31) $CO_2(g) + H_2O \rightleftarrows H_2CO_3$

The program predicts the equilibrium vapor pressure of SO_2, CO_2, and H_2O for the CaO-MgO-Na_2O-SO_2-SO_3-CO_2-N_2O_5-HCl-H_2O system. It also predicts liquid-solid equilibrium for $CaCO_3$, $CaSO_3$, $CaSO_4$, $Ca(OH)_2$, $MgCO_3$, $MgSO_3$, and $Mg(OH)_2$.

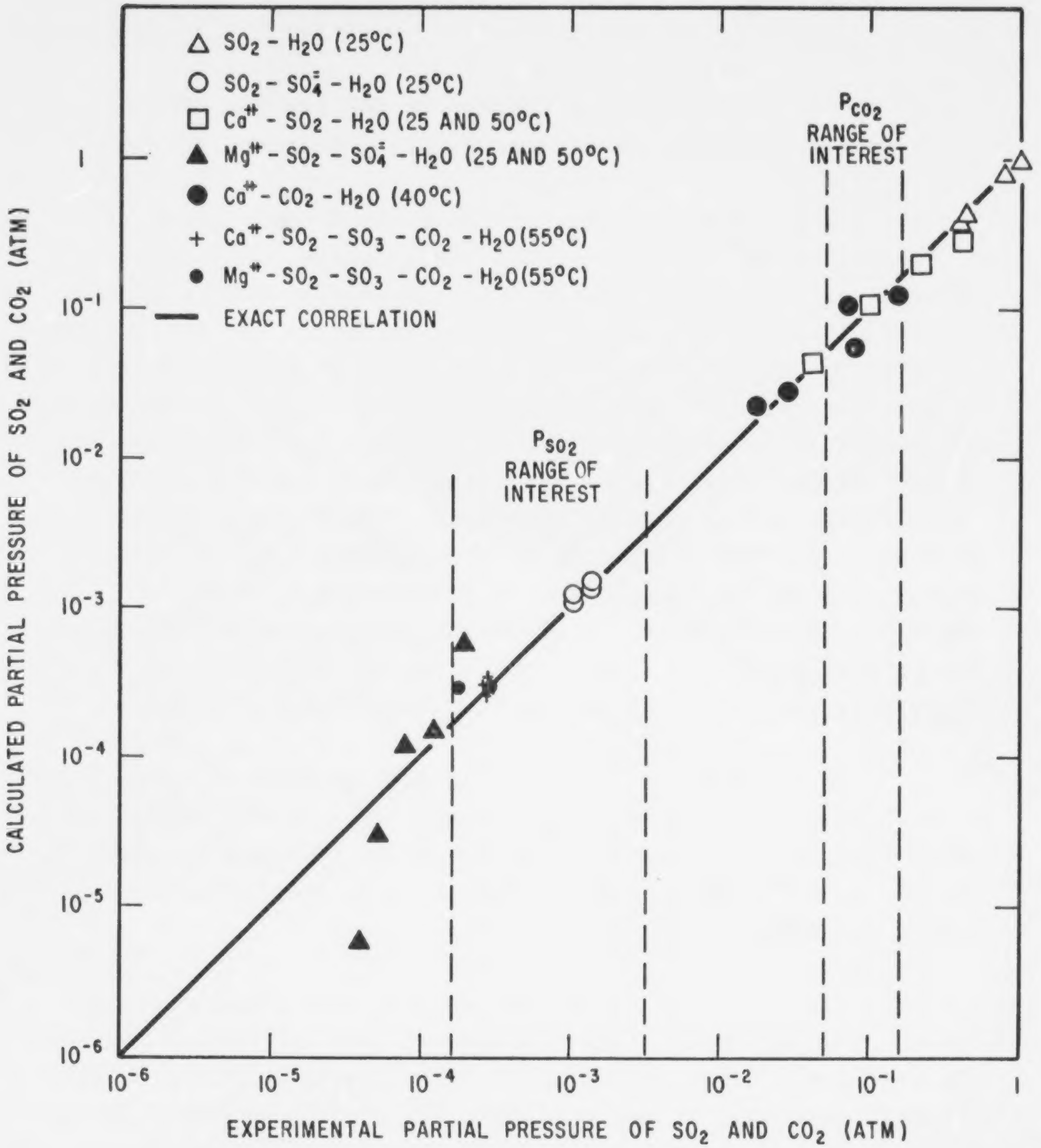
The accuracy of the equilibrium program in predicting the vapor pressures of SO_2 and CO_2 is shown in Figure 4. These data are in the temperature range of 25 to 55°C and represent ionic strengths up to 1.5.

3.2 Equipment Operating Characteristics

The open literature was surveyed to obtain information concerning the important operating characteristics for the various pieces of process equipment. The scrubber is the primary area of concern here. As mentioned earlier, the scrubber serves as a gas-liquid contacting device with some dissolution of lime and/or limestone solids.

Two scrubber types were considered: (1) countercurrent contactors, such as the turbulent contact absorber and the marble-bed contactors, and (2) cocurrent contactors, such as venturi scrubbers.

The turbulent contact absorber (TCA), designed and manufactured by Universal Oil Products Company, Air Correction Division, is a moving bed of hollow plastic spheres. The marble-bed contactor (Hydro-filter), manufactured by National Dust Collector Corporation, uses a bed of glass marbles instead of hollow spheres. Combustion Engineering, Inc., has installed two commercial scrubber systems using marble-bed units. In each of these scrubber types, the liquid-solid bed is characterized by violently turbulent action. Both of these scrubbers will be



FIGURF 4 - COMPARISON OF CALCULATED AND EXPERIMENTAL PARTIAL PRESSURES OF SO_2 AND CO_2 FOR THE SYSTEMS STUDIED tested in demonstration runs planned by OAP for the LIWS process on TVA's Shawnee Power Plant near Paducah, Kentucky.

Experimental data reported by B. H. Chen and W. J. M. Douglas (CH-003) show that the liquid-phase dispersion observed in a 12-inch diameter TCA unit corresponds to approximately 1.12 ideally backmixed vessels in series for the liquid and gas flow rates considered important in the LIWS process. No experimental data concerning the residence time distribution of the liquid phase in marble-beds has been reported. The present Radian model assumes that the liquid phase in both of these contactors is ideally backmixed. The implication of this assumption is that the liquid in the scrubber has the same composition as the liquid leaving the scrubber. Thus, if vapor-liquid equilibrium is closely approached in the contactor, the partial pressure of SO_2 in the exit gas will be equal to the vapor pressure of SO_2 above the exit liquid.

H. R. Douglas, et al., (DO-001) studied SO_2 absorption by NaOH solutions in a pilot TCA contactor. If the liquid flow is approximately backmixed as indicated by Chen and Douglas, the SO_2-NaOH scrubbing system appears to be very close to vapor-liquid equilibrium.

In cocurrent contactors such as the venturi, the gas leaving the scrubber is last in contact with the liquor leaving the scrubber. Thus, as above, if vapor-liquid equilibrium is closely approached in the scrubber, the partial pressure of SO_2 in the exit gas will be equal to the vapor pressure of SO_2 of the exit liquor. Experimental results on a pilot Venturi scrubber (LO-027) indicate that vapor-liquid equilibrium is not closely approached, however.

The scrubber effluent hold tank is a well-agitated mixing tank that allows time for CaO to hydrate, $Ca(OH)_2$ to dissolve, and sulfite and sulfate solids to precipitate. This stirred tank should approximate idealized backmixed flow and in practice should be designed to provide enough residence time and agitation to hydrate and dissolve the major portion of the CaO and MgO that reacts in the system. In a properly designed system, a major portion of the precipitation will occur in the effluent hold tank.

The clarifier and filter function primarily as solid-liquid separators. If the scrubber effluent hold tank is designed to accommodate most of the solid-liquid mass transfer, very little additional reaction should occur in the rather stagnant clarifier. The process water hold tank is essentially another completely mixed tank where make-up water is added and some additional hydration, dissolution, and precipitation can occur.

3.3 Model Formulation

The Radian process model described in this paper is based upon several simplifying assumptions.

(1) The partial pressures of SO_2, CO_2, and H_2O in the stack gas leaving the scrubber are in equilibrium with the scrubber liquid at the scrubber temperature (vapor-liquid equilibrium is achieved and the gas leaving the scrubber is last in contact with liquid having the composition of the scrubber exit liquor).

(2) After withholding a portion of the input lime (CaO and MgO) as being chemically unreacted in the system, solid-liquid equilibrium is achieved in the scrubber-effluent and process-water hold tanks.

(3) Hold tanks closely approach idealized backmixed vessels.

(4) The clarifier and filter are solid-liquid separators only (no chemical change occurs).

(5) Ionic reactions taking place in the liquid phase are rapid and thus are at equilibrium.

With the present absence of reliable rate data, the extent of reaction for the remaining "rate controlling" steps is specified by model input. That is to say, the fraction of limestone solids in the inlet flue gas entering the scrubber and dissolving, sulfite oxidizing, NO_x absorbing, and solids in the scrubber feed dissolving are set by model parameters. Thus, this version of the Radian process model is appropriately termed a "fractional conversions" process model.

The compositions for the system inlet and exit streams [limestone (LS), fly ash (FA), flue gas (FG), stack gas (SG), and water make-up (WM)] and operating conditions for the process are also specified by model parameters.

Process simulations are conducted by specifying the amount of SO_2 to be removed from a flue gas of known composition and adjusting the amount of slurry recycle (or the amount of scrubber feed in some cases) to obtain this SO_2 removal.

All of the liquid-phase species are allowed to react in the scrubber. However, as mentioned above, the fractions of limestone solids reacting in the scrubber and the fractions of various solid species in the scrubber feed that are available for reaction are specified as model inputs. Thus, for a fixed scrubber feed (SF) rate, the amount of slurry recycle (SR) required to obtain the desired SO_2 removal is a measure of the scrubbing efficiency of the process liquid. High slurry recycle rates indicate a poor set of scrubbing parameters.

4.0 SIMULATION RESULTS

A number of simulations have been conducted for the LIWS wet scrubbing scheme depicted in Figure 2. Simulation results showing the effects of (1) sulfite oxidation, (2) ionic strength, (3) limestone amount and composition, and (4) scrubber feed rate will be presented here. More recently, a limestone tail-end wet scrubbing system with essentially the same flow arrangement was simulated. In this instance, limestone was added to the process water hold tank instead of entering with the flue gas. Observations concerning the basic difference between lime and limestone systems will be presented later.

4.1 Sulfite Oxidation

The effect of sulfite oxidation on the operation of the limestone wet scrubbing process is shown in Table II. Here the percent oxidation was varied from 0 to 90% for a system

TABLE II

EFFECT OF SULFITE OXIDATION

QUANTITY	CASE NUMBER PSN19	PSN13	PSN18	PSN2B	PSN15
SULFITE OXIDATION, %	0	10	30	50	90
SCRUBBER L/G (GAL/1000 ACF)	13.4	14.0	14.0	14.0	14.0
SLURRY RECYCLE/SCRUBBER FEED RATIO	0	0.208	0.577	0.710	0.819
$m_{FB}[CaSO_3 \cdot 1/2H_2O(S)]$	5.34	4.80	3.73	2.65	0.52
$m_{FB}[CaSO_4(S)]$	0.00	0.52	1.59	2.64	4.70
$m_{SF}[\text{Total } SO_2]$	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}
$m_{SF}[\text{Total } SO_3]$	0.00	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}
$(pH)_{SB}$	4.37	4.30	4.20	4.06	3.39

utilizing a pure $CaCO_3$ limestone. The scrubber liquid-to-gas ratio was maintained at 14 gallons of scrubber feed per 1000 ACF of flue gas, except for the 0% oxidation case. In this case, only 13.4 gal/1000 ACF were needed for 90% SO_2 removal from a 2000 ppm SO_2 flue gas. As the percent oxidation increases from 10 to 90% the fraction of slurry recycle required in the scrubber feed progressively increases from 0.208 to 0.819. This loss of scrubbing efficiency with increased oxidation is evidently caused by the formation of the strongly acidic sulfuric acid (the pH of the scrubber bottoms stream is lowered).

Of course oxidation changes the type of solids leaving the system. As expected, the amount of calcium sulfite solid leaving the system in the filter bottoms (FB) stream progressively decreased with oxidation while the amount of calcium sulfate increased. The concentrations of sulfites and sulfates in solution do not follow this trend, however, since they are controlled by solubility relationships.

4.2 Ionic Strength

The effect of ionic strength for systems injecting a pure $CaCO_3$ limestone is given in Table III. The ionic strength of the scrubbing solution was varied from 0.48 up to 1.00 by the addition of sodium chloride to the model. This would correspond to different degrees of fly ash solubility in the actual process. For the cases presented here, the effect of ionic strength on scrubbing efficiency was fairly minor. As the ionic strength increased from 0.48 to 1.00, the fraction of slurry recycle required in the scrubber feed only increased from 0.710 to 0.733. This increase can be explained in terms of the total concentration of basic species dissolved in the scrubber feed liquid. Here basic species are defined as all

TABLE III

EFFECT OF IONIC STRENGTH

QUANTITY	CASE NUMBER PSN2B	 PSN23	 PSN20
IONIC STRENGTH	0.48	0.75	1.00
SCRUBBER L/G (GAL/1000 ACF)	14.0	14.0	14.0
SLURRY RECYCLE/SCRUBBER FEED RATIO	0.710	0.717	0.733
LIQUID-PHASE MOLALITIES OF SF			
OH^-	1.56×10^{-2}	1.50×10^{-2}	1.38×10^{-2}
$CaOH^+$	1.17×10^{-2}	1.14×10^{-2}	1.11×10^{-2}
$CaSO_3(\ell)$	2.59×10^{-4}	2.48×10^{-4}	2.38×10^{-4}
NaOH (ℓ)	1.95×10^{-4}	6.39×10^{-4}	1.04×10^{-3}
All Basic Species	2.78×10^{-2}	2.73×10^{-2}	2.62×10^{-2}
Ca^{++}	1.14×10^{-1}	1.21×10^{-1}	1.27×10^{-1}
ACTIVITY COEFFICIENT OF SF SPECIES			
Ca^{++}	0.238	0.226	0.228
OH^-	0.721	0.744	0.784
$SO_3^=$	0.188	0.157	0.139

species capable of liberating a hydrogen ion due to the first ionization of sulfurous acid. For the cases presented in Table III, the sum of the basic-species molalities in the scrubber feed decreases from 2.78×10^{-2} to 2.62×10^{-2} g-moles/kilogram H_2O as the ionic strength increases.

Although the sum of the basic-species molalities does not change much in this instance, the individual molalities and activity coefficients do vary significantly over the ionic strength range shown with OH^-, $CaOH^+$ and $CaSO_3(\ell)$ decreasing while $NaOH(\ell)$ increased. The deviation of activity coefficients from the ideal value of unity demonstrates their need in these aqueous equilibrium calculations and suggests their consideration in rate correlations. The significant variation of individual molalities and activity coefficients with ionic strength suggests that other regions of system operation may exist whereby ionic strength will have a significant effect on scrubbing efficiency.

4.3 Limestone Amount and Composition

The effect of limestone amount and composition is shown in Table IV. In cases PSN2B and PSN4B, 112.5% of the limestone required for 100% SO_2 removal was considered available for reaction in the system. Case PSN2B corresponds to a process injecting limestone containing a negligible amount of MgO, whereas Case PSN4B corresponds to a process injecting limestone containing 20 mole percent of reactive MgO. To remove 90% of the SO_2 in a flue gas containing 2000 ppm SO_2, 71.0% of the scrubber feed was slurry recycle in Case PSN2B. On the other hand, Case PSN4B required the scrubber feed to be 87.7% slurry recycle.

TABLE IV

EFFECT OF LIMESTONE AMOUNT AND COMPOSITION

	CASE NUMBER			
QUANTITY	PSN2B	PSN4B	PSN21	PSN22
LIMESTONE AVAILABLE, % THEORETICAL	112.5	112.5	135	135
LIMESTONE COMPOSITION, % MgO	0	20	0	20
SCRUBBER L/G, GAL/ 1000 ACF	14	14	14	14
SLURRY RECYCLE/SCRUBBER FEED RATIO	0.710	0.877	0.510	0.510
FILTER SOLIDS STREAM				
pH	11.3	8.4	11.3	11.3
IONIC STRENGTH	0.48	0.70	0.48	0.48
m_{FBL}(Total CaO)	$1.5x10^{-1}$	$2.2x10^{-2}$	$1.5x10^{-1}$	$1.5x10^{-1}$
m_{FBL}(Total MgO)	0	$2.4x10^{-1}$	0	$9.1x10^{-7}$
$m_{FBS}[Ca(OH)_2]$	$9.6x10^{-1}$	0	2.16	$6.1x10^{-1}$
$m_{FBS}[Mg(OH)_2]$	0	1.14	0	1.59
% SO_3 AS LIQUID SULFATE	0.36	4.54	0.37	0.36
% MgO AS $Mg(OH)_2$	--------	82.69	--------	99.99+

An explanation of this observation is possible when the nature of the scrubbing liquid is examined for Cases PSN2B and PSN4B. Enough calcium oxide has been added to the system in PSN2B so that the scrubbing liquor becomes a saturated solution with respect to calcium hydroxide (pH = 11.3) and $Ca(OH)_2$ leaves the system as a solid in the waste solid. However, all of the calcium is utilized in PSN4B (no $Ca(OH)_2$ in the waste solids) so that the scrubbing liquor becomes saturated with respect to magnesium hydroxide (pH = 8.4). The preliminary conclusion here is that a calcium-based scrubbing liquor is capable of more scrubbing than the calcium plus magnesium-based liquor.

If the amount of limestone available for reaction is increased (refer to Case PSN21 for a 100% CaO system and Case PSN22 for an 80% CaO-20% MgO system), the amount of slurry recycle required to remove 90% of the SO_2 in a 2000 ppm flue gas is reduced. In fact, for both cases PSN21 and PSN22, only 51.0% slurry recycle is required. The reduction in amount of slurry recycle for both cases is expected since with more limestone available the solid contains more calcium and magnesium hydroxide. (The simulation cases are run with a specified fraction of $Ca(OH)_2$ and $Mg(OH)_2$ dissolving in the scrubber.) The fact that cases PSN21 and PSN22 require the same amount of slurry recycle can be explained again by examining the composition of the scrubbing liquor. It turns out that enough CaO is added in PSN22 so that the scrubbing liquor is saturated with respect to $Ca(OH)_2$. Thus the liquid phase of Cases PSN2B, PSN21, and PSN22 are almost the same. The molality of total magnesium species in the liquid phase for Case PSN22 is only 9.1×10^{-7} g-moles per kilogram of liquid water. Almost all of the magnesium (99.99+%) leaves the system as $Mg(OH)_2$ solid in Case PSN22, whereas only 82.7% leaves as $Mg(OH)_2$ solid in Case PSN4B.

For the calcium plus magnesium-type scrubber liquid (PSN4B), the ionic strength of process liquor is 0.70 g-moles per kilogram H_2O as compared to 0.48 for calcium-type liquids (PSN2B, PSN21, PSN22). Of course, this would be expected since magnesium species are more soluble. Along the same line, 4.54% of the sulfate leaves the system in the liquid phase for Case PSN4B. Less than 1% of the sulfate leaves in the liquid phase for the calcium-type liquids. The amount of sulfate leaving the system as a liquid would continue to increase as more magnesium and less calcium is made available to the process.

4.4 Scrubber Feed Rate

The effect of scrubber feed rate is shown in Table V. Here the cases shown in the first two data colums are the same as those shown in Table IV, i.e., PSN2B and PSN4B. Cases PSN11 and PSN12 were made based upon high scrubber feed rates. In the system using a pure $CaCO_3$ limestone (PSN11), 20 gal/1000 ACF of scrubber feed containing no slurry was sufficient to remove 90% of the SO_2 from a 2000 ppm flue gas. In a system using an 80 mole% CaO - 20 mole% MgO limestone (PSN12), 87.2% slurry recycle was required at a scrubber feed rate of 21 gal/1000 ACF. This can be explained in terms of the amount of basic species dissolved in the calcium-based and calcium plus magnesium-based scrubbing solutions.

Comparison of Cases PSN2B and PSN11 indicates that the liquid-phase of the scrubber feed has made a significant contribution toward absorbing SO_2 in the scrubber. On the other hand, comparison of PSN4B and PSN12 indicates that the liquid-phase for Ca plus Mg-based scrubbing solutions is not as potent. In the Ca plus Mg-based cases, dissolution of the

TABLE V

EFFECT OF SCRUBBER FEED RATE

QUANTITY	CASE NUMBER PSN2B	PSN4B	PSN11	PSN12
LIMESTONE COMPOSITION, % MgO	0	20	0	20
SCRUBBER L/G, GAL/ 1000 ACF	14	14	20	21
SLURRY RECYCLE/SCRUBBER FEED RATIO	0.710	0.877	0.00	0.872
Wt.% SOLIDS IN SF	2.1	6.0	0.01	3.8
Wt.% SOLIDS IN SR	2.9	6.9	0.0	4.3
m_{SF} (BASIC SPECIES IN LIQUID)	2.8×10^{-2}	2.0×10^{-3}	2.7×10^{-2}	2.6×10^{-3}
m_{FBS} $[Ca(OH)_2]$	0.96	0	0.57	0
m_{FBS} $[Mg(OH)_2]$	0	1.14	0	1.10
FRACTION CO_2 ABSORBED	5.2×10^{-4}	2.4×10^{-4}	1.4×10^{-3}	3.5×10^{-4}

SF solids in the scrubber account for a major portion of the scrubbing. These remarks are supported by (see Table V): (1) the amount of solids in the scrubber feed stream (weight per unit time) is about the same for Cases PSN4B and PSN12 and (2) the concentration of basic species in solution is approximately 10 to 15 times as much for the Ca-based solutions as for the Ca plus Mg-based solutions (refer to the molalities of basic species in the SF liquid shown in Table V).

4.5 LTEA Versus LIWS

A comparison of the limestone tail-end addition (LTEA) process with the limestone injection wet scrubbing (LIWS) process is shown in Table VI. Cases PSN2B and PSN11 are simulations for the LIWS process using a pure CaO limestone feed. Cases PSN32 and PSN34 are the LTEA simulations corresponding to Cases PSN2B and PSN11, respectively. In Cases PSN2B and PSN32, the scrubber L/G was set to 14 gal/1000 ACF and the fraction of solids dissolving in the scrubber was set to 0.35. In Cases PSN11 and PSN34, the slurry recycle was set to zero. It was found that the desired SO_2 removal was obtained by feeding 20 gal of SF/1000 ACF of FG for Case PSN11 and 72.7 gal/1000 ACF for Case PSN34. Case PSN33 is a LTEA simulation corresponding to Case PSN32 except that only 0.10 of the basic solids were allowed to dissolve in the scrubber. This case was run to take into account the fact that limestone is generally not as reactive as lime.

Comparison of Cases PSN2B and PSN32 indicates that approximately 6% more slurry recycle was required to converge the LTEA case (SR/SF = 0.752) than was required for the LIWS case (SR/SF = 0.710). This would indicate that if a relatively high fraction of solids dissolve in the scrubber (0.35), not much more slurry recycle would be required for the LTEA process

TABLE VI

COMPARISON OF LIWS AND LTEA PROCESSES

			CASE NUMBER		
QUANTITY	PSN2B	PSN32	PSN33	PSN11	PSN34
PROCESS TYPE	LIWS	LTEA	LTEA	LIWS	LTEA
SCRUBBER L/G (GAL/1000 ACF)	14.0	14.0	14.0	20.0	72.7
FRACTION SOLIDS DISSOLVING IN S	0.35	0.35	0.10	0.35	0.35
SLURRY RECYCLE/SCRUBBER FEED RATIO	0.710	0.752	0.950	0.00	0.00
SF STREAM PROPERTIES					
WT. % SOLIDS	2.1	2.8	16.5	0.01	0.07
m_{SFL} (OH-)	$1.6\text{x}10^{-2}$	$2.2\text{x}10^{-6}$	$3.5\text{x}10^{-8}$	$1.5\text{x}10^{-2}$	$5.8\text{x}10^{-8}$
m_{SFL} (ALL BASIC SPECIES)	$2.8\text{x}10^{-2}$	$2.7\text{x}10^{-4}$	$2.7\text{x}10^{-4}$	$2.7\text{x}10^{-2}$	$2.7\text{x}10^{-4}$
FB STREAM PROPERTIES					
pH	11.3	5.7	5.7	11.3	5.9
IONIC STRENGTH	0.48	0.50	0.50	0.48	0.50
m_{FBL} (TOTAL CaO)	$1.5\text{x}10^{-1}$	$1.5\text{x}10^{-1}$	$1.5\text{x}10^{-1}$	$1.5\text{x}10^{-1}$	$1.5\text{x}10^{-1}$
m_{FBL} (TOTAL CO_2)	$4.1\text{x}10^{-6}$	$1.2\text{x}10^{-2}$	$1.2\text{x}10^{-2}$	$4.1\text{x}10^{-6}$	$5.5\text{x}10^{-3}$
m_{FBL} (TOTAL SO_2)	$2.7\text{x}10^{-4}$	$4.8\text{x}10^{-4}$	$4.5\text{x}10^{-4}$	$2.7\text{x}10^{-4}$	$4.0\text{x}10^{-4}$
m_{FBL} (TOTAL SO_3)	$9.6\text{x}10^{-3}$	$9.5\text{x}10^{-3}$	$9.5\text{x}10^{-3}$	$9.6\text{x}10^{-3}$	$9.5\text{x}10^{-3}$
FRACTION CO_2 ABSORBED	$5.2\text{x}10^{-4}$	$-1.27\text{x}10^{-2}$	$-1.27\text{x}10^{-2}$	$1.4\text{x}10^{-3}$	$-1.27\text{x}10^{-2}$

than for the LIWS process. This is because a major portion of the basicity available in the scrubber is being provided by solids dissolution.

If a major portion of the basicity in the scrubber needs to be provided from the liquid-phase, the LTEA process does not appear as attractive as does the LIWS process. This is demonstrated by examining the results of PSN33, PSN11, and PSN34. Comparison of Cases PSN11 and PSN34 shows that nearly four times (72.7 ÷ 20) scrubber feed must be used in the LTEA when no slurry recycle is utilized. This is because the circulating liquors in LIWS processes (essentially lime liquors) contain approximately 100 times as much basic species as do LTEA processes. In Case PSN11 (LIWS), the sum of the molalities of the basic species is 0.027 g-moles/kg H_2O. In Case PSN34 (LTEA), the sum is 0.00027 g-moles/kg H_2O.

Case PSN33 shows the effect of a lowered value for the fraction of solids dissolving. In Case PSN33, the slurry recycle to scrubber feed rate ratio is 0.950 and the weight percent solids in the scrubber feed is 16.5%. In Case 32, the SR/SF ratio is only 0.752 and the weight percent solids is only 2.8. Thus, if the limestone is less reactive than lime (as expected), the SR/SF ratio (and thus the weight percent solids) must be increased to provide the necessary basicity.

It should be noted here that the above discussion does not quantify the effect of the difference in reactivities of lime and limestone. This comparison requires a correlation of the dissolution rates in the scrubber environment. It is generally agreed that properly calcined limestone is more reactive than raw limestone. The above discussion indicates that the LTEA process is more dependent upon solids dissolution in the scrubber since LTEA liquors contain less basic species than do LIWS liquors.

Further comparison of the LTEA cases with the LIWS cases shows that (1) the liquor pH's are less for the LTEA process, (2) the ionic strengths are approximately the same, (3) the molalities of total CaO, total SO_2, and total SO_3 in the effluent liquor (FB liquor) are approximately the same, and (4) the molality of total CO_2 in the effluent liquor is much larger for the LTEA process. As would be expected, the LTEA process desorbs CO_2 in the scrubber as contrasted to the absorption of CO_2 in the LIWS process.

5.0 SUMMARY

Radian has developed a mathematical description of lime/limestone wet scrubbing processes. Vapor-liquid-solid equilibrium for the $CaO\text{-}MgO\text{-}Na_2O\text{-}SO_2\text{-}SO_3\text{-}CO_2\text{-}N_2O_5\text{-}HCl\text{-}H_2O$ system has been described on a thermodynamically sound basis. Numerical results based upon equipment descriptions and process assumptions were calculated. The following conclusions have been drawn based upon these simulation results.

(1) Scrubbing solutions originating from high calcium limestones are more efficient than those originating from dolomites.

(2) Sulfite oxidation reduces the SO_3 scrubbing efficiency of the wet scrubbing process.

(3) Ionic strength has an effect on the concentration of basic species in solution and thus the scrubbing efficiency.

(4) LIWS process (lime) liquors contain more basic species in solution than do LTEA

process (limestone) liquors. Thus, in LTEA processes where the less reactive raw limestone is the additive, either higher liquor rates or weight percent solid slurries must be utilized to obtain comparable SO_2 removals.

The lime/limestone wet scrubbing model presented here can easily be adapted to other scrubbing processes containing the same chemical species. Although the model described in this paper is based upon certain equilibrium assumptions and the specification of fractional conversions for rate limiting steps, this model provides an excellent basis for process design and development studies, particularly in the areas of (1) determining the technical feasibility of process alternatives, (2) estimating process flow rates and compositions, and (3) correlating experimental data.

As rate data become available, the model can be revised to include the proper rate correlations. Since v-ℓ-s equilibrium has been described in terms of the activities of individual ions or ion pairs, these rate correlations can be properly expressed in terms of the activities of the various reacting species and the distance from thermodynamic equilibrium.

ACKNOWLEDGEMENTS

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PRECIPITATION KINETICS OF $CaSO_4 \cdot 2H_2O$

By:
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Presented at:

SECOND INTERNATIONAL LIME/LIMESTONE
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Sheraton-Charles Hotel
New Orleans, Louisiana

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1.0 INTRODUCTION

Precipitation of solid products is an important aspect of lime or limestone wet scrubbing process design. Process performance and operability are directly related to several solid-liquid mass transfer rates. Radian Corporation, under contract to the Office of Air Programs (Contract No. 68-02-0023); is conducting laboratory studies intended to characterize precipitation kinetics of $CaSO_4 \cdot 2H_2O$ and $CaSO_3 \cdot \frac{1}{2}H_2O$. This paper presents results of tests conducted to date for the $CaSO_4 \cdot 2H_2O$ portion of the study.

2.0 PROCESS IMPLICATIONS OF PRECIPITATION KINETICS

The overall reaction for SO_2 removal in limestone wet scrubbing processes may be written

$$SO_2(g) + CaCO_3(s) + \frac{x}{2} O_2(g) \rightarrow (1-x)CaSO_3(s) + xCaSO_4(s) + CO_2(g)$$

Even though removal of SO_2 is accomplished by absorption in alkaline liquid, the ultimate products must be solid $CaSO_3$ or $CaSO_4$ in order for waste disposal to be feasible. Thus in order to precipitate a solid product, supersaturated conditions must be intentionally maintained at some point in the process. A workable process design must solve the problem of promoting precipitation in one process vessel or waste disposal area while preventing or controlling it in others.

In the development of almost any industrial process, data characterizing important fundamental aspects of process chemistry and kinetics may not be available. A decision then must be made regarding the best method of developing a reliable and economically feasible process design. Process development activities may be generally divided into bench scale, pilot scale, and full scale tests. A proper blend of these activities must be selected to result in a successful development over a reasonable period of time.

For example, full scale tests of a process are ultimately necessary to demonstrate process operability. On the other hand, field conditions may make it virtually impossible to gather meaningful design information. Extrapolation of the design to new operating conditions may then be difficult and risky. A pilot plant offers an improved opportunity to control and measure process variables as compared to a full scale operation. At the same time, care must be taken to insure that pilot plant results are applicable to the full scale design. A similar situation exists with respect to laboratory or bench scale studies. Such work may be capable of producing accurate and valuable data if means are available to apply this information to a full scale design.

In process development then, one must

a. select those aspects of the process that are most suitably studied at the bench, pilot, and full scale levels;

b. develop a design scheme capable of applying laboratory and pilot scale data to a full scale installation.

Precipitation kinetics are one area of limestone scrubbing process design that is suitable for laboratory study. It is a vital aspect of the process. Careful measurements under controlled conditions are necessary to draw meaningful conclusions. Laboratory determination of the form of rate constants and driving force terms can be applied to full scale process design. Laboratory values of the rate constants may be used for full scale design although values determined in a pilot plant would probably be more meaningful.

3.0 THEORY

Precipitation processes are in general a combination of two rate steps, nucleation and growth. Nucleation is the process by which a small solid particle first forms in a supersaturated solution. Once this nuclei has formed, it will grow at some rate. In many supersaturated systems growth will occur in the absence of nucleation when crystal seeds are introduced into the solution. It is the intention of this study to characterize the growth step rather than the nucleation step of precipitation kinetics.

The bulk volumetric crystal growth rate can be conveniently written as the product of a rate constant k, a term M dependent in some way upon the amount of seed present (such as mass, area, or number) and Φ, a "driving force" term which is some function of solution composition. Thus,

$$\text{Growth Rate} = kM\Phi \quad \text{moles liter}^{-1}\text{min}^{-1}$$

If the growth rate were limited by a chemical reaction at the crystal surface, k should be a relatively strong function of temperature only. If the rate of diffusion of ions to the crystal surface is important, k may also be a function of agitation, particle size, and solution composition.

In previous investigations of precipitation kinetics the driving force function Φ was commonly expressed in terms of the difference between the actual concentration of a salt in a liquor and the equilibrium or saturated concentration. This often led to satisfactory correlation of experimental data. In the case of limestone scrubbing systems, however, a simple driving force function such as this cannot be applied.

First of all, the precipitating ions are not present in stoichiometric amounts. Process simulations have shown, for example, that when a high calcium limestone is used, the ratio of Ca^{++} to $SO_4^=$ in solution may be more than 10:1. Secondly, limestone scrubbing liquors have a relatively high ionic strength so that the activities of ions in solution differ significantly from their concentrations. This behavior makes calculation of "supersaturation" a complicated function of solution composition. Finally, several ion pairs including $CaSO_4$ and $MgSO_4$ are present in solution in significant amounts so that perhaps 50% of total CaO and SO_3 in a liquor is not in the form of the Ca^{++} and $SO_4^=$ ions that are precipitating.

These factors make a rather sophisticated computation of individual ion activities a necessity for correlating precipitation kinetics in limestone scrubbing liquors. Under previous contract to OAP, Radian Corporation has developed a computer routine for performing the necessary calculations. This computational scheme in its most general form also enables laboratory kinetics data to be applied directly to full scale process design problems.

The immediate objectives of the present study are:

a. determination of the product kM and its dependence on temperature, agitation, and amount of seed;

b. determination of the driving force function Φ in terms of individual ion activities and equilibrium solubility constants.

4.0 EXPERIMENTAL

A schematic of the apparatus used to study $CaSO_4 \cdot 2H_2O$ precipitation rates is shown in Figure 4-1. Supersaturated solutions are produced by introducing two separate feed solutions (e.g., $CaCl_2$ and Na_2SO_4) into a single well-stirred reactor. Feed rates are carefully set and controlled automatically. The reactor is situated in a constant temperature bath held at the desired experimental temperature. A given amount of seed crystals is introduced into the reactor at the beginning of each run. A filter membrane is fixed across the reactor outlet to contain the seed within the reactor. Since the volume of seed crystals does not increase significantly during the course of a run, a steady-state material balance may be written for the reactor for either CaO or SO_3*. Thus,

$$\left(F_{SO_3} \times C_{SO_3}\right)_{\text{inlet}} - \left(F_{SO_3} \times C_{SO_3}\right)_{\text{outlet}} = \text{Rate of Precipitation}$$

Rate of SO_3 entering Reactor

Rate of SO_3 leaving Reactor

The rate is calculated directly by measuring the feed and effluent flow rates and concentrations $\left(F_{SO_3} \text{ and } C_{SO_3}\right)$.

The steady state concentration of reactant may be varied by either varying mean residence time or feed compositions.

---

*The term "CaO" refers to total calcium in solution. "SO_3" means total sulfur in the +6 oxidation state. This will be distributed among various species such as HSO_4^-, $SO_4^=$, etc. The symbol $SO_4^=$ means that particular ionic species.

EXPERIMENTAL SYSTEM FOR
PRECIPITATION RATE STUDY

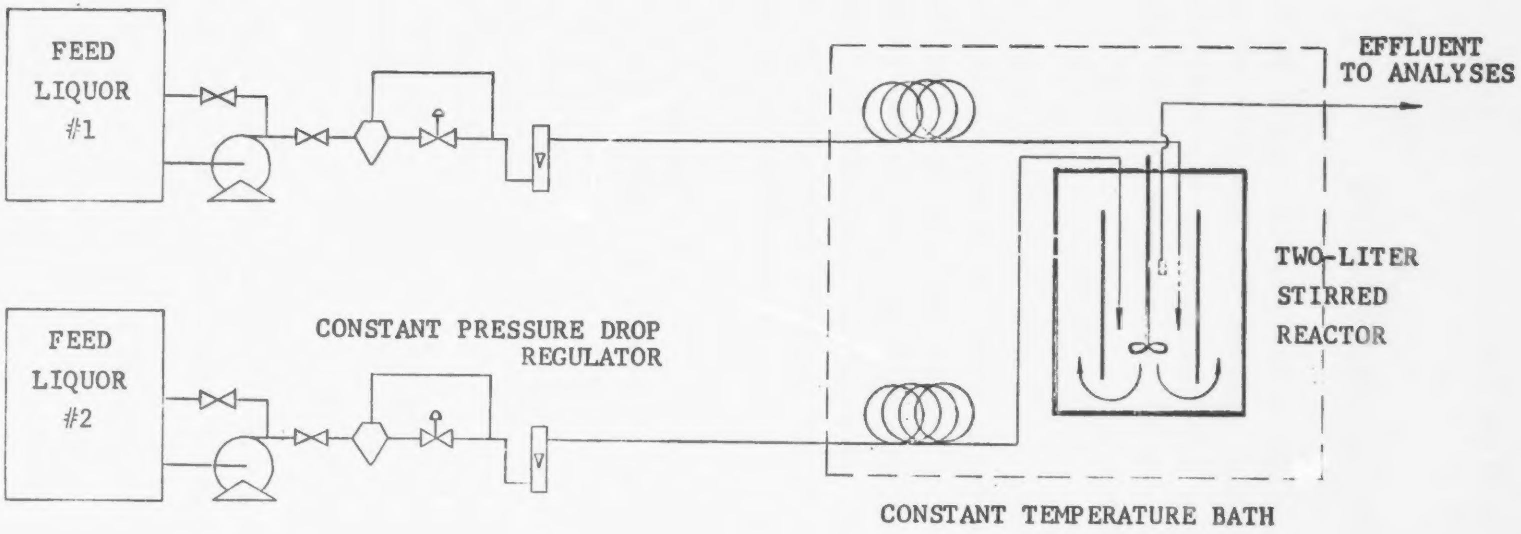


FIGURE 4-1

5.0 RESULTS AND DISCUSSION

In Figure 5-1 precipitation rate R in millimole liter^{-1} min^{-1} is plotted against the quotient of activity product $a_{Ca^{++}}a_{SO_4^=}$ and solubility product K_{sp} for the case where $a_{Ca^{++}} \cong a_{SO_4^=}$. Figure 5-2 shows a similar plot for the nonstoichiometric case, $a_{Ca^{++}}/a_{SO_4^=} \cong 20$.

The rate curves appear to incorporate two distinct regions. At relatively low supersaturations, the rate is linear with calculated values for the activity product of Ca^{++} and $SO_4^=$ ions. At higher supersaturations the growth rate rises very sharply above this linear correlation. Comparative photomicrographs of seed and product crystals show that this departure from a linear driving force is due to nucleation.

Figure 5-3 shows a photograph of $CaSO_4 \cdot 2H_2O$ seed crystal used for these experiments. This seed was prepared from a mixture of $CaCl_2$ and Na_2SO_4 solutions and screened to + 325 mesh. Figures 5-4a and 5-4b show product crystals from two of the stoichiometric precipitation experiments. Figure 5-4a corresponds to precipitation in the low supersaturation region and 5-4b the high region. In both cases, large regular crystals have grown from the seed. Some smaller nuclei are apparent in 5-4b however.

Figures 5-5a and 5-5b show products from two nonstoichiometric runs at low and high supersaturation respectively. In both cases, a number of smaller crystals has formed. Again, however, the high supersaturation case shows a much greater amount of nucleation than the lower case. Clearly, two factors influence the amount of nucleation markedly. As the supersaturation increases beyond a certain

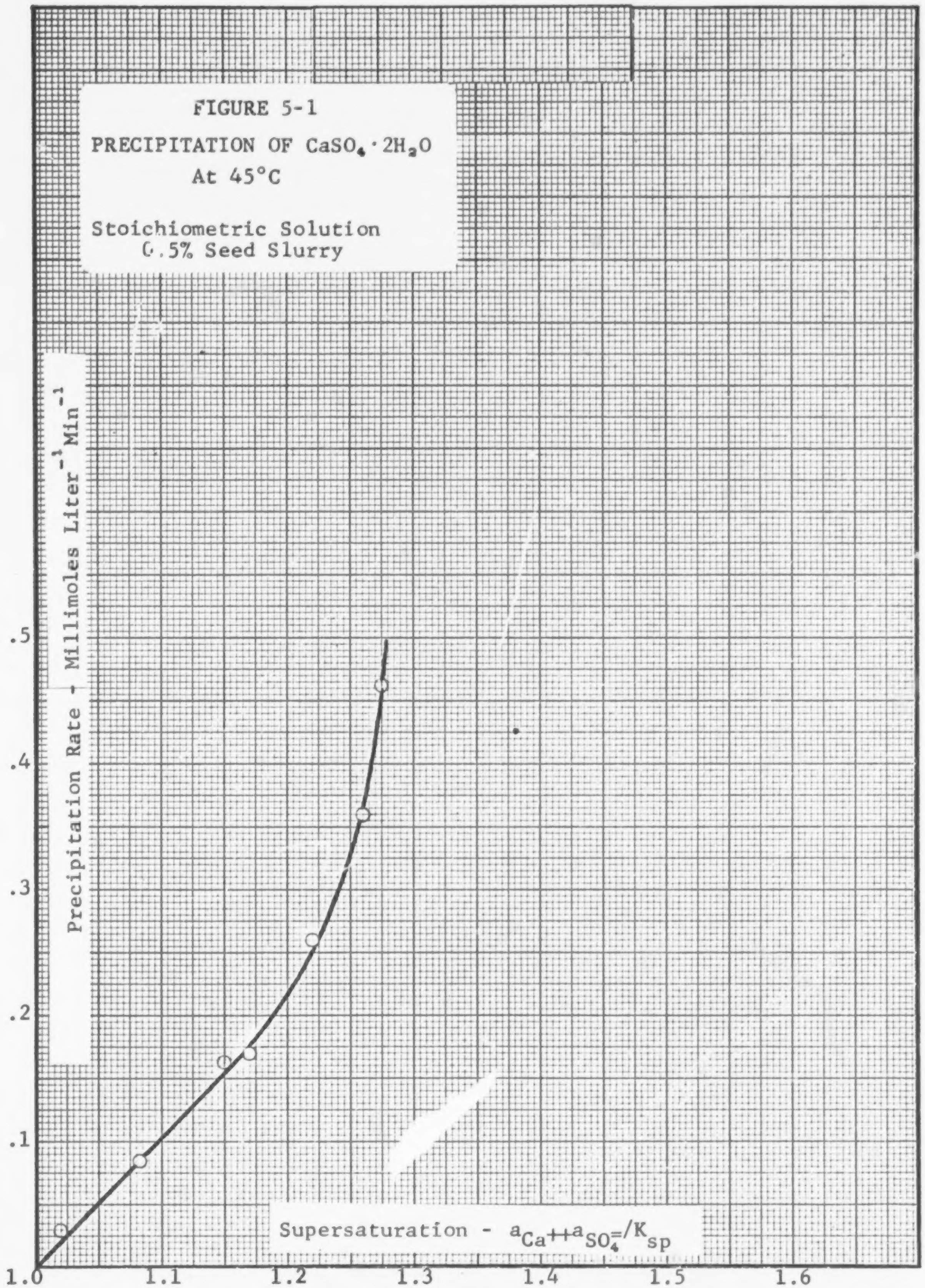


FIGURE 5-1

PRECIPITATION OF $CaSO_4 \cdot 2H_2O$

At 45°C

Stoichiometric Solution

0.5% Seed Slurry

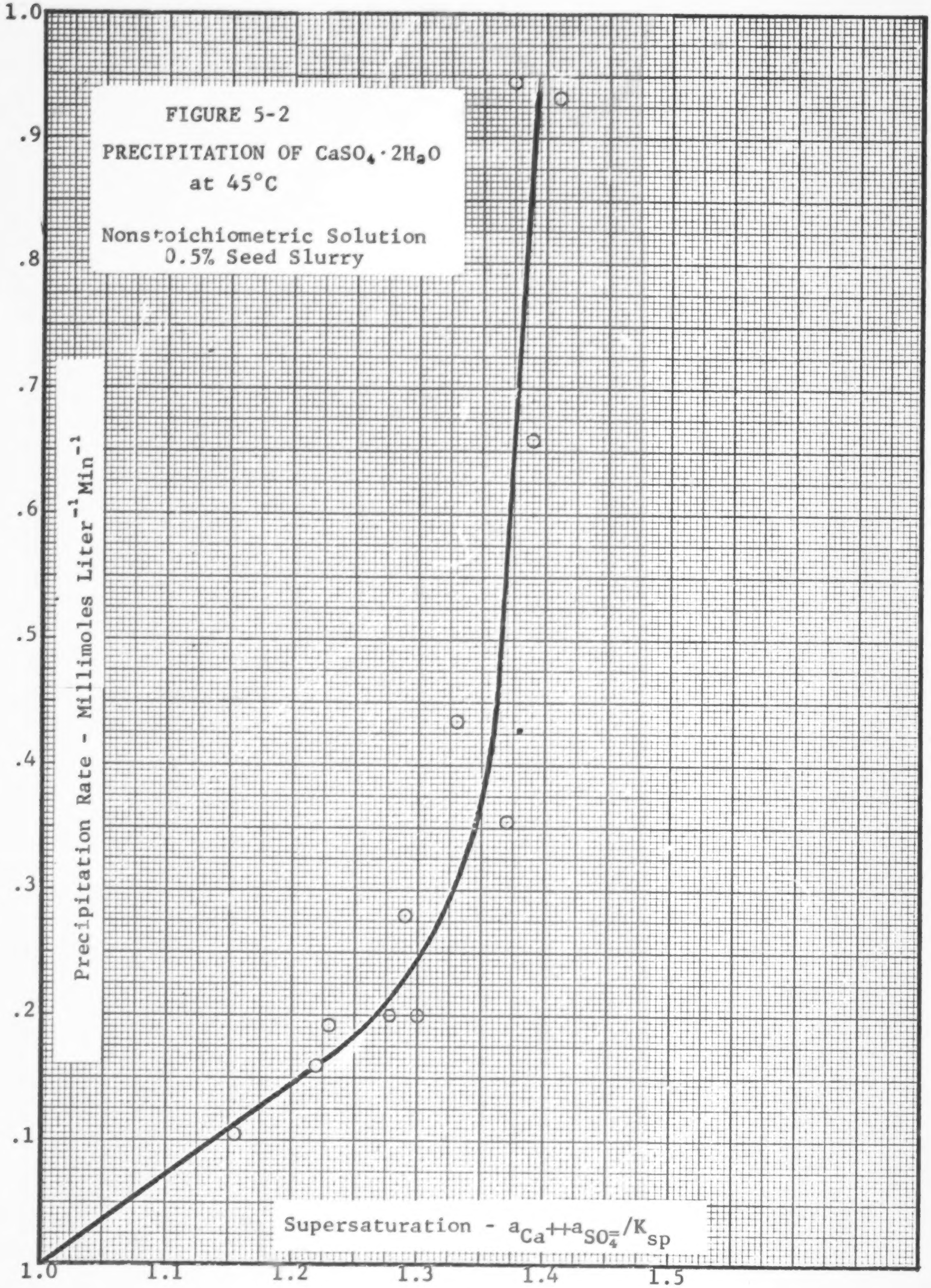
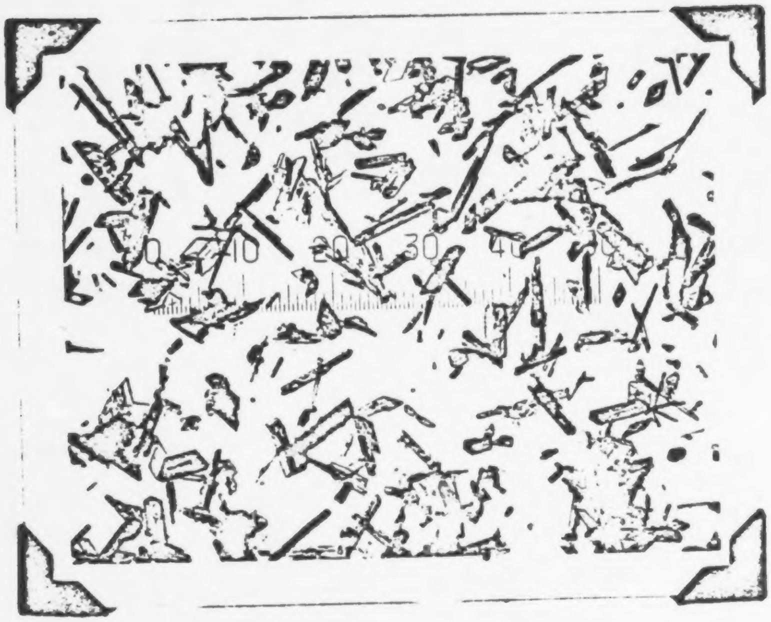


FIGURE 5-2

PRECIPITATION OF $CaSO_4 \cdot 2H_2O$ at 45°C

Nonstoichiometric Solution
0.5% Seed Slurry

K&E 10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.



0-50 = 500 Microns

FIGURE 5-3

SEED CRYSTALS FOR $CaSO_4 \cdot 2H_2O$ PRECIPITATION EXPERIMENTS

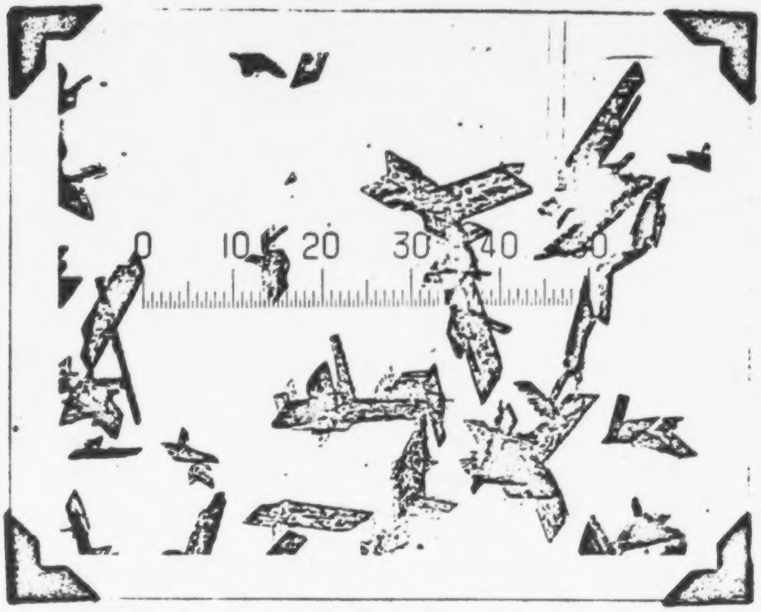


FIGURE 5-4a - PRODUCT CRYSTALS FROM STOICHIOMETRIC RUN AT LOW SUPERSATURATION

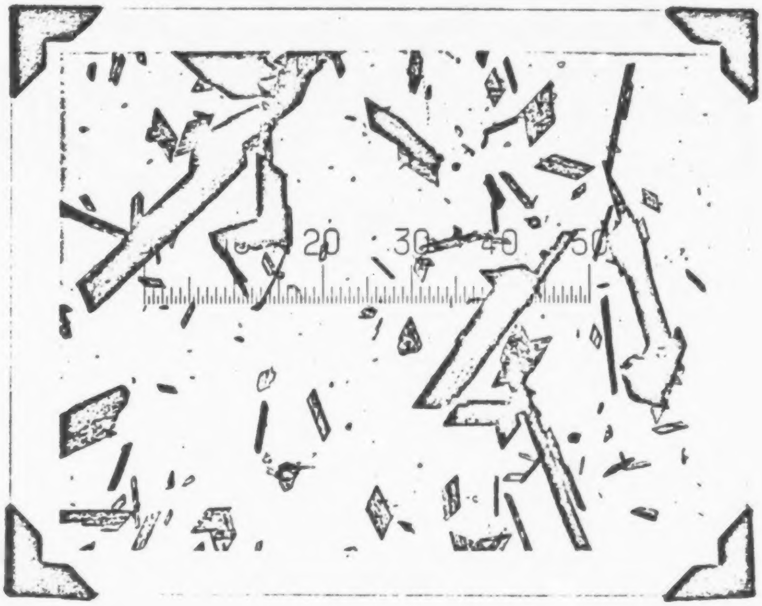


FIGURE 5-4b - PRODUCT CRYSTALS FROM STOICHIOMETRIC RUN AT HIGH SUPERSATURATION

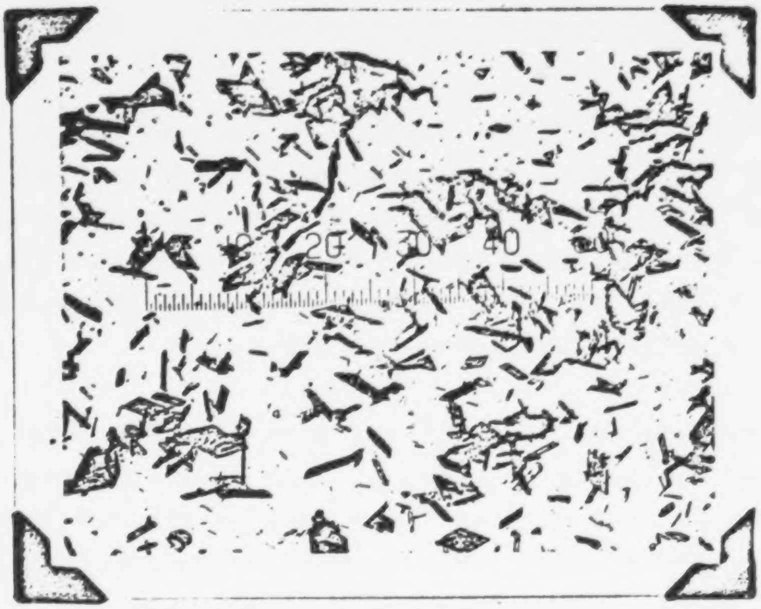


FIGURE 5-5a - PRODUCT CRYSTALS FROM NONSTOICHIOMETRIC RUN AT LOW SUPERSATURATION

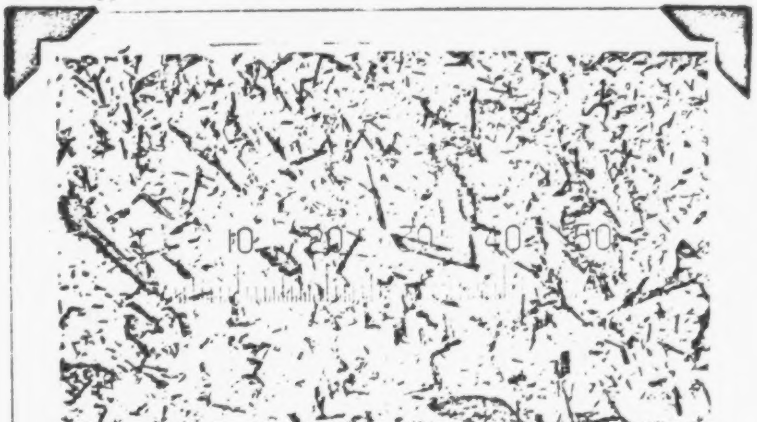


FIGURE 5-5b - PRODUCT CRYSTALS FROM NONSTOICHIOMETRIC RUN AT HIGH SUPERSATURATION

level, nucleation increases rapidly. Also, as the ratio of Ca^{++} to $SO_4^=$ ions in solution increases, nucleation increases. For a given ratio of $Ca^{++}/SO_4^=$ the level of supersaturation at which nucleation becomes important can be expressed quantitatively as a ratio of calculated ion activity product to the solubility product at a particular process temperature.

This behavior could have significant impact on limestone scrubbing process design. As mentioned before, supersaturated conditions must exist in some portion of limestone scrubbing processes in order for solid waste precipitation to be accomplished. Furthermore, in a closed-loop system (desirable from the standpoint of avoiding waste water treatment) all of the process streams except perhaps the vessel where make-up water is introduced, will be at or near saturation. This means that an operable closed loop process will require that the flow sheet be designed so that all process streams are maintained in or below the region of supersaturation where nucleation is negligible. The ability to design such a process requires:

a. chemical and thermodynamic information characterizing equilibrium conditions in limestone scrubbing processes;

b. quantitative data describing precipitation rates as a function of process stream composition and temperature;

c. a design oriented computational scheme incorporating these precipitation rate correlations.

To illustrate the importance of an accurate formulation of the process chemistry and thermodynamics, the precipitation data shown in Figures 5-1 and 5-2 have been replotted in Figure 5-6. Here, the precipitation rates have been correlated using physically measurable quantities, total CaO and total SO_3 in solution. Even though the stoichiometric and nonstoichiometric cases are self consistent on this plot, two completely different rate curves result when the ratio of CaO to SO_3 changes. Obviously these results would be quite misleading if used for process design calculations.

Recall, on the other hand, that the data correlated using calculated ion activities show similar behavior for precipitation rates even over this great range of solution compositions. Thus, one could confidently extrapolate these data to a variety of process design conditions.

6.0 CONCLUSIONS

The following can be concluded from work completed to date.

- For the $CaSO_4 \cdot 2H_2O$ system, a region of supersaturation exists where nucleation is negligible.
- Within this region, the precipitation rates of $CaSO_4 \cdot 2H_2O$ are proportional to the activity product of Ca^{++} and $SO_4^{=}$.
- Properly correlated precipitation rate data can be extrapolated over a wide range of liquor compositions.

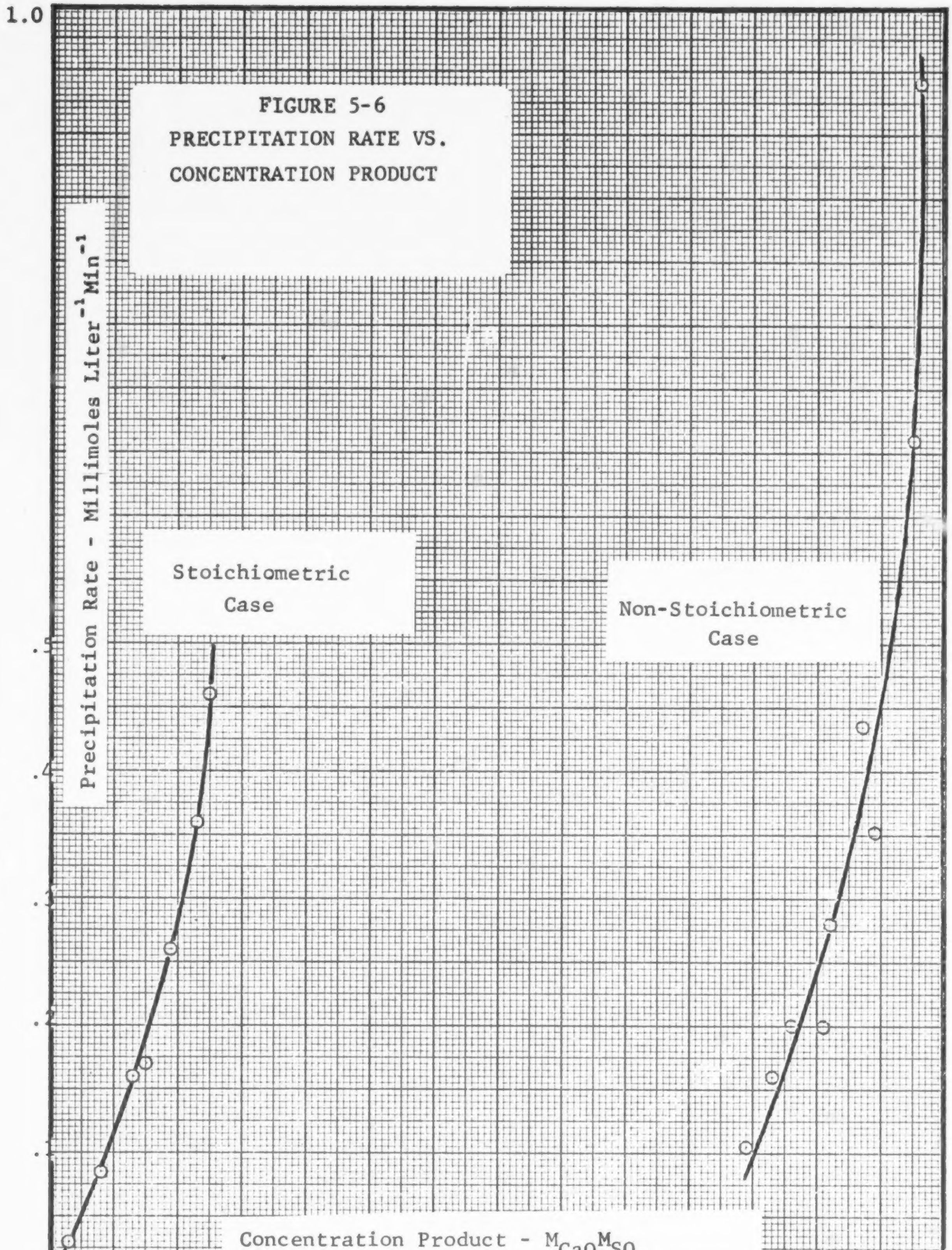


FIGURE 5-6
PRECIPITATION RATE VS.
CONCENTRATION PRODUCT

K+E 10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

LIMESTONE TYPES FOR FLUE GAS SCRUBBING

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Prepared for
Lime/Limestone Wet Scrubbing Symposium
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LIMESTONE TYPES FOR FLUE GAS SCRUBBING

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Abstract

Limestones vary dramatically in their reactivity as bases. Optimization of limestone scrubbing processes will involve selection of a limestone or carbonate rock type. This work compares carbonate rock types as to their dissolution rates in acid media and as to their sulfur oxide removal efficiencies in a batch scrubber.

It was found that dissolution rates of limestones could vary by a factor of ten while dissolution rates of calcined limestone and scrubbing efficiencies of calcined and uncalcined limestones could vary by a factor of five. Whether calcined or uncalcined, the best of the carbonate rock types tested for batch scrubbing efficiency were marl and chalk. The worst were marble and magnesite. The dissolution rates of limestones were markedly greater at lower pH but were an order of magnitude lower than that of calcined limestone.

For calcined limestone, the change in scrubbing efficiency with calcination temperature was a function of the change in surface area or pore volume. At higher calcination temperatures where surface area was lost, reactivity was lost. The variance in scrubbing efficiency with different calcined limestone types was a function of both the surface area and pore volume.

Limestone Types for
Flue Gas Scrubbing

Introduction

In response to the demand for control of air pollution, a great many scrubbing processes have been proposed and investigated(1). Approximately $200 million were spent last year on scrubber design and construction. However, a process most likely acceptable to the utility industry would not involve operation of chemical recovery equipment. Lime and limestone scrubbing processes not only meet this requirement but also promise high SO_2 and particulate removals efficiencies(2,3). Since limestones vary dramatically in their reactivity(4), optimization of these processes will involve selection of a limestone or limestone type.

The purpose of the work presented in this report was to delineate the possible effect of limestone type on scrubbing efficiency. To this end, dissolution rates and batch scrubber tests were conducted using both calcined and uncalcined carbonate rocks. Twelve basic carbonate rock types were selected for this study. The first nine types correspond identically to the nine types of Dr. R. D. Harvey(5). Types 10, 11, and 12 correspond to Georgia marble (#1336), Michigan marl (#2129), and Kansas chalk (#2081), respectively. One additional limestone was investigated for effects of calcination temperature on scrubbing performance. This fine grained oolitic stone (#2061) was calcined at several temperatures from 1700°F to 3200°F. The physical properties and reactivity of these calcines have been discussed in a previous study(6). Complete petrographic and chemical analysis of all of the carbonate rocks used in this study has been given by Harvey and is summarized in Table 1.

Procedure

1. Dissolution Rate of Limestones in H_2SO_3

Two approaches were taken to determine the dissolution rate of limestones in sulfurous acid. The first procedure referred herein as acid washing allowed 1.8N sulfurous acid to trickle through a thin bed of 5.0 grams of 16/20 mesh sample placed between filter paper in a buchner funnel at room temperature. The reacted acid was collected in 50 ml portions of the original 200 ml of acid. The calcium concentration of each portion was determined wet chemically and then divided by the time required for passage of that portion of acid through the sample. The resulting number giving the weight of calcium per time is divided by the weight of sample dissolved per time. After comparison of this value for each portion, these weight dissolution rates were averaged and divided by the appropriate equivalent weight.

The second procedure was called dissolution rate at constant pH. A 1 g. sized mesh sample is slurried in 200 ml of distilled water and titrated with 0.21 N sulfurous acid. The titration rate is continuously adjusted to bring the slurry pH down to the desired pH and then to hold it there. Quantities of acid consumed at minute intervals were recorded and the equivalents of acid consumed per time were calculated. Since the buret used to deliver the acid and the beaker which held the slurry were water jacketed, desired timperatures of interest could be selected.

2. Dissolution Rate of Calcined Limestone in H_2SO_3

Dissolution rates for calcines could not be determined in exactly the same fashion as they were for carbonates because dissolution for calcines was too rapid. Consequently, a modified procedure of the Eckhard coarse grain acid titration test was developed. In this method 1 gram of sized sample is slurried in 200 ml of distilled water and titrated at minute intervals with sulfurous acid to pH 7. From these data a curve of cumulative acid consumed versus time is drawn. In order to have a numerical estimate of the dissolution rate during the initial portion of the curve, the predicted consumption of acid at one minute from the smooth curve was used to compute the equivalents of acid consumed per time and volume.

3. Flue Gas Scrubbing with Calcined and Uncalined Limestone

Both limestone and lime were tested for their effectiveness as flue gas scrubbing additives using the same apparatus (see Figure 1). The apparatus consisted of a 1-liter temperature regulated batch scrubber and a small side vessel (approximately 250 ml); total volume of the system was 1500 ml. The liquor was continuously circulated between the scrubber and side vessel at 3 liters/minute. Flue gas with 3000 ppm SO_2 was bubbled through the liquid in the batch scrubber at 10 SCFH. A Beckman 315 IR was used to monitor the effluent SO_2 concentration and pH was measured with a probe in the side vessel. After an initial period of bubbling flue gas through the scrubber liquid, the effluent SO_2 concentration would stabilize at a concentration slightly below the SO_2 concentration in the flue gas.

At this time approximately one half gram of limestone or one quarter gram of lime (weight necessary for 0.01 alkaline equivalents) was added to the side vessel and the change in effluent SO_2 concentration and pH are recorded. The reduction in SO_2 would rapidly reach a peak and gradually fall to zero. The peak reduction in SO_2 concentration due to the addition of 0.01 alkaline equivalents of sized sample was reported.

Results

1. Dissolution Studies

Dissolution rates of carbonates as determined by acid washing and by titration at constant pH are given in Table 2 for the ISGS types of carbonate rocks. These data were obtained for 16/20 mesh material at 70°F. The ranking of dissolution rates by acid washing is 11 > 2 > 1 > 3, 4, 9 > 10 > 5, 6 or marl > calcite > marble > dolomite. The effect of particle size on these data is illustrated in Figure 2. The ranking of dissolution rates at a constant pH 4 is 11 > 8 > 3, 4 > 1, 2 > 10 > 5, 9 > 7 or marl > aragonite > calcite > marble > dolomite > magnesite. The effects of pH level, solution temperature, and particle size are shown in Figures 3, 4, and 5. Dissolution doubled if the pH were one unit lower or the temperature 40°F higher. Particle size had little effect for marl.

Dissolution rates of calcined carbonate rocks were estimated from an acid titration procedure as described above and are given in Table 3. These data were obtained at 70°F for 1 gram of 42/65 mesh stone calcined at 2000°F. The ranking for estimated dissolution rates of oxides is 1, 8 > 5, 11, 12 > 2, 3, 4 > 6, 9, 10 > 7 or aragonite and spar > chalk and marl > calcite > dolomite and marble > magnesite. The effects of calcination temperature and particle size are illustrated in Figures 6 and 7. These rates include the rate of hydration and the effect of hydration on particle size. Hence, they may reflect hydration and decrepitation rates more than "dissolution".

2. Flue Gas Scrubbing

Results for the peak reduction in SO_2 concentration due to the addition of 0.01 alkaline equivalents of carbonate rock in the batch scrubber are shown in Table 4. Since the amount of alkali added is small, the peak reduction in ppm of SO_2 is only an index of reactivity and not a predictor for absolute scrubber efficiency. The ranking of carbonate rock types at 120°F solution temperature using 150/170 mesh material is 11 > 12 > 2 > 1, 9 > others > 7 or marl > chalk > calcite > others > magnesite. Raising solution temperature from 90°F to 150°F only slightly improved the performance of the marl while decreasing particle size increased it sharply (see discussion of results).

Addition of 0.01 alkaline equivalents of oxides (2000°F calcines) gave a clear ranking in reactivity using a 150/170 sample (see Table 4). At 110°F solution temperature, this ranking is 11 > 12 > 9 > 1, 4 > others or marl > chalk > clacitic dolomite > calcite > others. Using 42/65 mesh sample, the performance of almost all the types was poor; marble and non reef dolomite gave no response at all. The effect of particle size was strongly dependent on carbonate rock type. For some the reactivity tripled or quadrupled by reducing the particle size while types 2, 3, and 8 (calcite spar, coarse grained limestone, and aragonite) showed no significant improvement.

Discussion of Results

1. Dissolution Rates

Analysis of dissolution rates by titration at constant pH was pursued extensively since these data were precise. In particular, information on the effect of temperature and pH were used to estimate the activation energy and order of the reaction. In Figure 8 is shown the dissolution rate data for stone #2203 (ISGS type 3) and Michigan marl #2129 (ISGS type 11) plotted against reciprocal absolute temperature. From this it was calculated that the activation energies for the reaction $CaCO_3$ (solid) $+ H_2SO_3$ (aq.) $\rightarrow$ solution at pH 6 are 5.14 k cal/gmole for Type 3 and 6.54 k cal/gmole for Type 11. By plotting dissolution rate data at 90°F against hydrogen ion concentration on log-log graph paper the order of the dissolution reaction was estimated. For type 3 the order of the reaction was determined to be 0.34; for type 11, 0.70.

2. Flue Gas Scrubbing

For 150/170 mesh material the most effective carbonate rocks were type 11, Michigan marl and type 12, Kansas chalk both as the carbonate and the oxide. After marl and chalk, the rankings of calcined and uncalcined carbonate rocks are not directly comparable, however, in general calcites performed better than dolomites.

For both carbonates and oxides, SO_2 sorption rises sharply with decreasing particle size. It is similar to the effect of particle size on dissolution rate by acid washing as shown in Figure 9. Dissolution rates determined by acid titration to maintain a constant pH were practically independent of particle size for type 11, Michigan marl. Another dissimilarity between dissolution rate at constant pH and peak SO_2 reduction in the batch scrubber is the effect of temperature. The dissolution rate doubled from 70 to 110°F while SO_2 reduction was weakly dependent on temperature over this range.

3. Correlation with Physical Properties

All samples tested for dissolution rate or flue gas scrubbing effectiveness were also analyzed by a contractor* for surface area by the B.E.T. method and pore volume using a mercury porosimeter. Correlation coefficients between dissolution rate or scrubbing effectiveness and physical properties were computed. Data for uncalcined carbonate rocks yielded only insignificant correlation coefficients. For calcined stone several correlations were observed. With calcination temperature as the parameter, the correlation coefficient for peak SO_2 reduction versus surface area is 0.99 and versus total pore volume is 0.98 (refer to Figure 10). This is in agreement with the previous study(6) that found strong correlations between surface area or pore volume and several measures of reactivity.

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* International Minerals and Chemicals

With carbonate rock type as the parameter, peak SO_2 reduction shows a dependence on both surface area and pore volume. As can be seen from Figure 11, variance in surface area predicts the variance in reactivity of the high calcium oxide stones except for marl and chalk. On the other hand, pore volume appears to account for the high reactivity of marl and chalk while the data for calcites remains somewhat scattered in Figure 12.

Conclusions

1. The most effective carbonate rock types for flue gas scrubbing using a batch reactor are Michigan marl and Kansas chalk irrespective of whether the comparison is among calcined or uncalcined stones.

2. The dissolution rates are a strong function of pH and most rapid at low pH. Dissolution doubles from 70°F to 110°F.

3. There are marked differences in the dissolution rates and scrubbing efficiencies among different types of stone (at least 5 times).

4. For calcined carbonate rocks, the change in scrubbing efficiency with calcination temperature is a function of the change in surface area or pore volume. At higher calcination temperatures where surface area is lost, reactivity is lost.

5. The variance in scrubbing efficiency with different calcined limestone types is a function of both the surface area and pore volume.

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Table 1: Chemical Analysis in Weight Percentage and Petrographic Characteristics

Sample Type Number	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	CO_2	Mineralogy*	Petrographic Type
1	Nil	Nil	Nil	Nil	55.3	43.95	Calcite	Iceland spar rhombs
2	Nil	0.01	0.19	Nil	55.5	43.35	Calcite	Spar
3	Nil	Nil	0.20	1.86	53.4	43.75	Calcite(dolomite)	Coarse limestone
4	1.53	0.01	0.31	0.00	54.8	43.35	Calcite(quartz)	Fine limestone
5	0.03	0.02	0.34	21.40	30.30	47.30	Dolomite	Reef dolomite
6	11.8	1.77	0.13	17.4	26.5	40.27	Dolomite(quartz, clay)	Nonreef (impure) dolomite
7	0.47	0.08	Nil	44.2	2.93	50.96	Magnesite	Fine magnesite
8	0.19	0.27	Nil	Nil	55.2	42.10	Aragonite	Oolitic sand
9	5.88	0.69	2.82	15.33	30.82	40.68	Dolomite(calcite, quartz)	Calcitic dolomite
10	0.85	0.20	0.15	1.4	53.7	43.4	Calcite(tremolite)	Marble
11	3.63	0.95	Nil	Nil	46.6	37.18	Calcite(quartz, clay)	Bog marl
12	2.48	1.09	0.15	1.41	51.4	39.44	Calcite	Chalk

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* Minor mineral constituents given in parenthesis

Table 2
Dissolution Rates* of Carbonate Rocks

Using 16/20 Mesh Sample

Type	Description	Acid Washing	Titration at Constant pH	
			pH=4	pH=6
1	Iceland Spar	1.54	0.12	0.00
2	Calcite Spar	3.29	0.10	0.00
3	Coarse grained limestone	1.08	0.27	0.15
4	Fine grained limestone	1.11	0.27	0.07
5	Reef Dolomite	0.45	0.04	0.00
6	Non reef dolomite	0.52	0.14	0.00
7	Magnesite		0.00	0.00
8	Aragonite		0.84	0.26
9	Calcitis dolomite	1.29	0.04	0.00
10	Marble	0.73	0.08	0.04
11	Marl	4.61	3.0	0.28

*in milli-equivalents per min per gram into volume of 200 milliliters

Table 3
Estimated Dissolution Rates of Calcined Carbonate Rocks *

Type	Description	Dissolution Rate meq/min/g
1	Iceland Spar	20
2	Calcite Spar	9
3	Coarse grained limestone	10
4	Fine grained limestone	12
5	Reef Dolomite	13
6	Non reef dolomite	6
7	Magnesite	4
8	Aragonite	25
9	Calcitis Dolomite	6
10	Marble	7
11	Marl	13
12	Chalk	15

*Calcined at 2000°F, 42/65 mesh

Table 4
Sulfur Dioxide Reduction* After Scrubbing Using 150/170 Mesh Sample

Type	Description	Uncalcined	Calcined at 2000°F
1	Iceland spar	450	450
2	Calcite spar	540	250
3	Coarse grained limestone	210	300
4	Fine grained limestone	225	400
5	Reef dolomite	250	—
6	Non reef dolomite	210	300
7	Magnesite	0	—
8	Aragonite	240	350
9	Calcitis dolomite	490	750
10	Marble	200	250
11	Marl	950	1150
12	Chalk	700	950

*sulfur dioxide concentration in parts per million in flue gas

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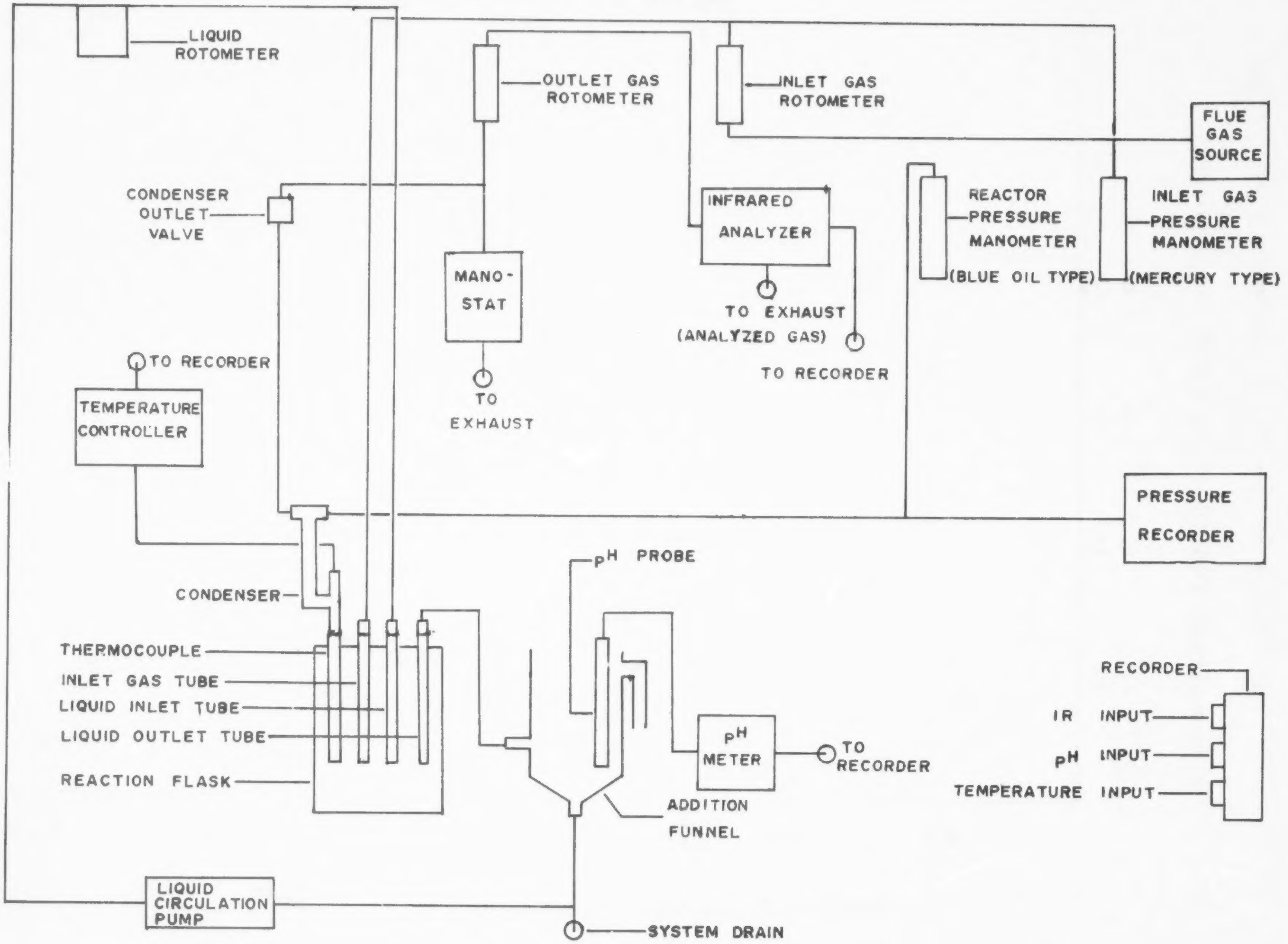
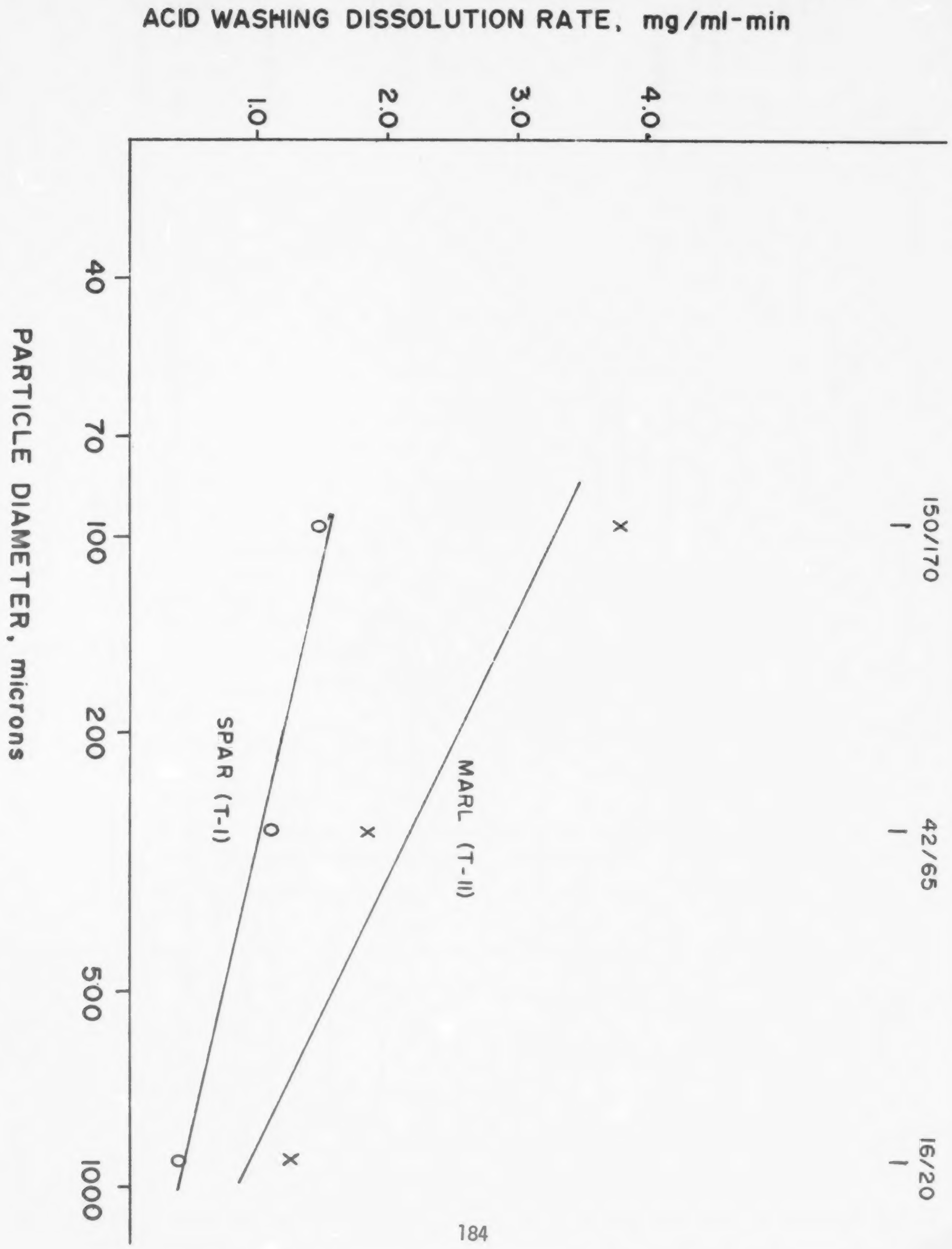
12. Correlation of SO_2 Reduction to Pore Volume for Different Calcined Limestones

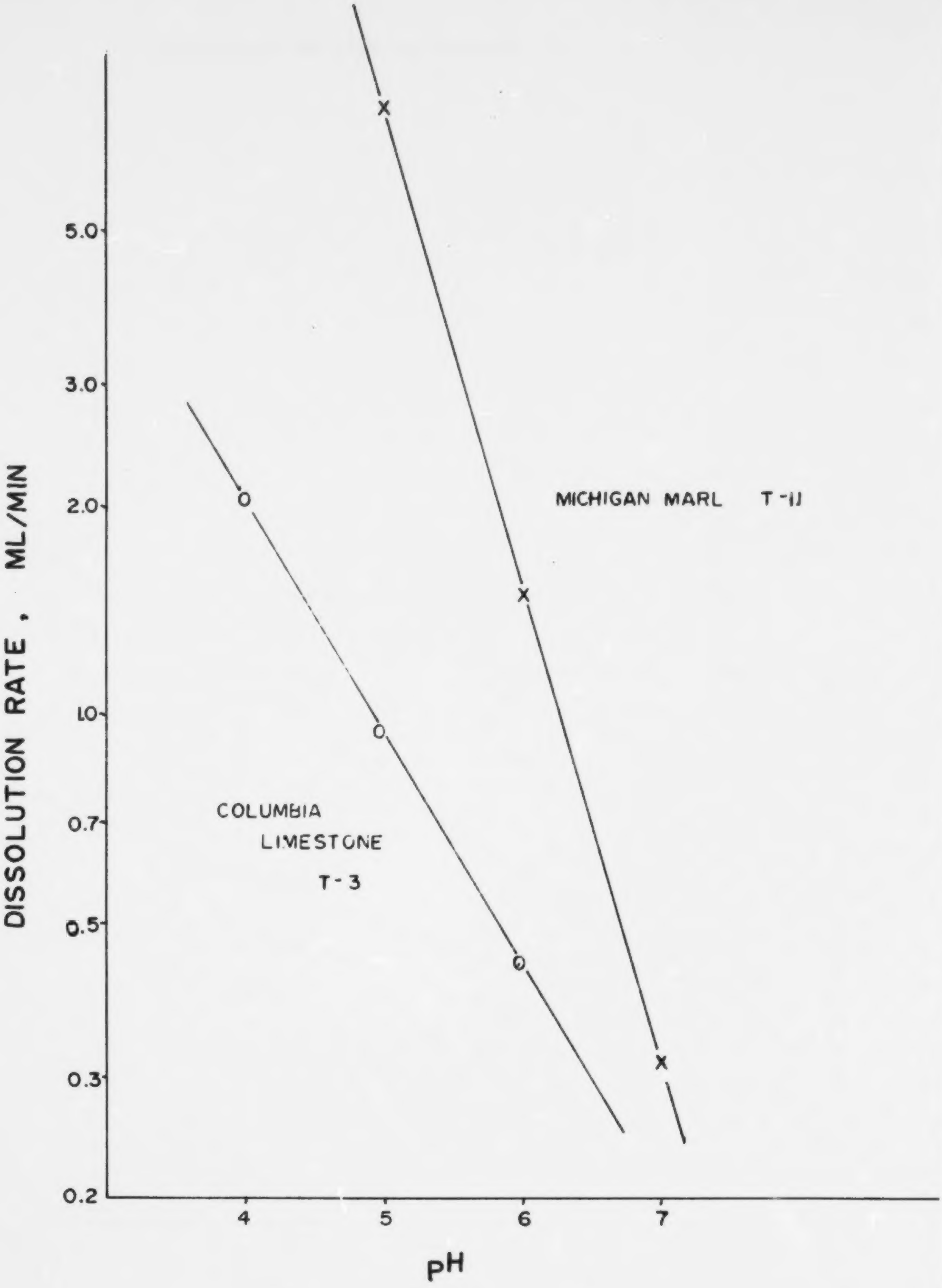
1. Batch Scrubbing Apparatus



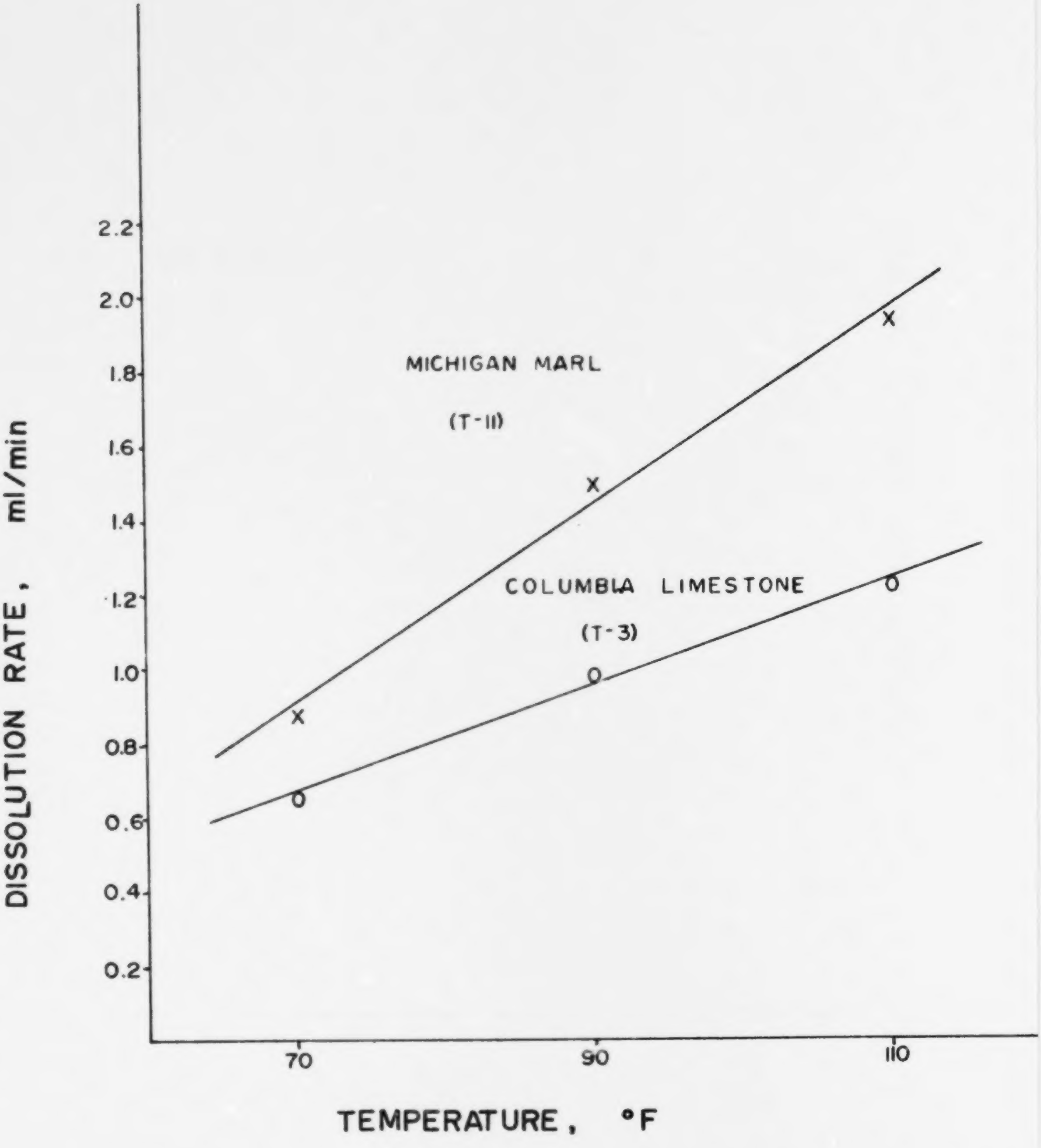
2. Effect of Particle Size on Acid Washing Dissolution Rate

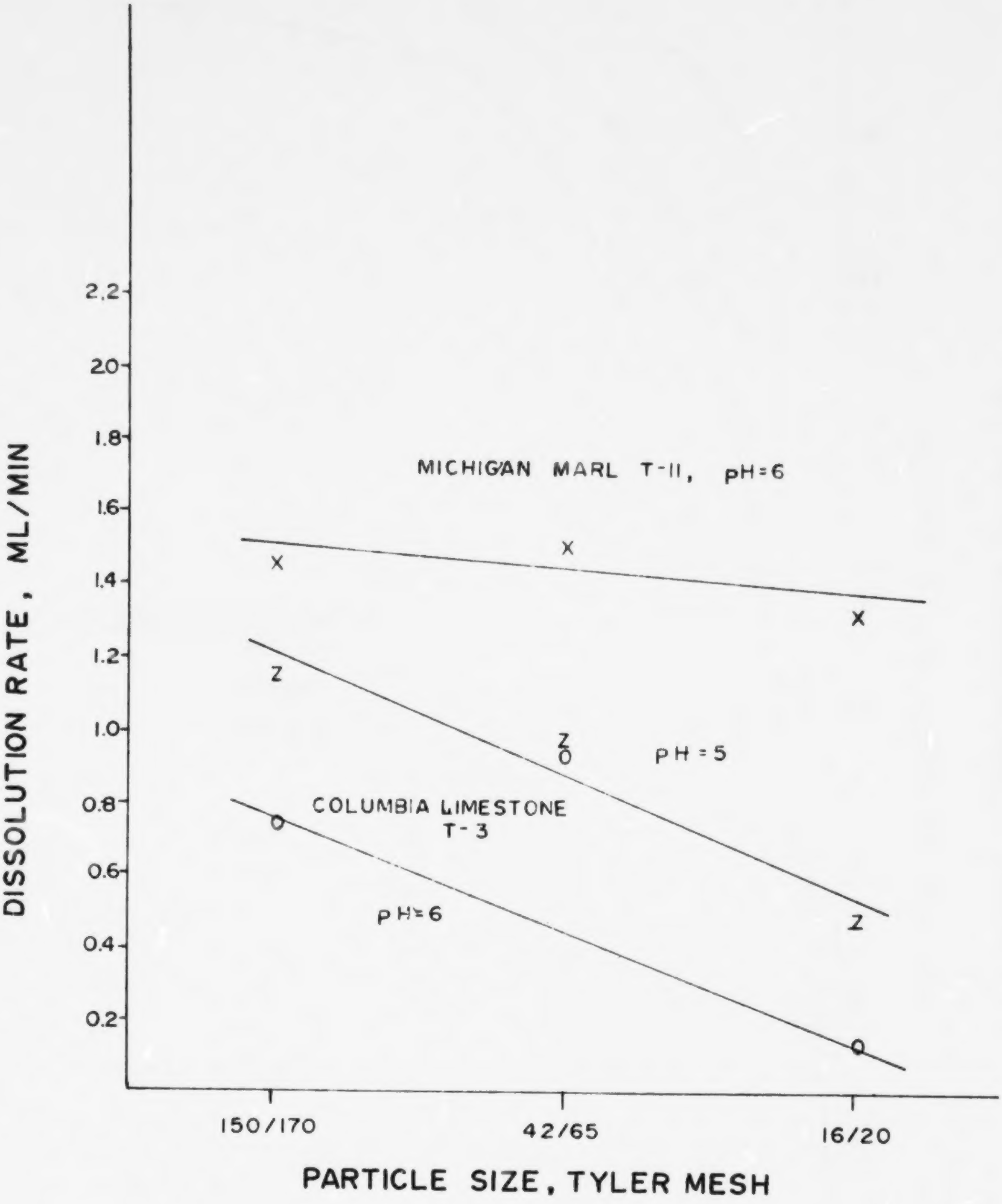


3. Dissolution Rate VS pH

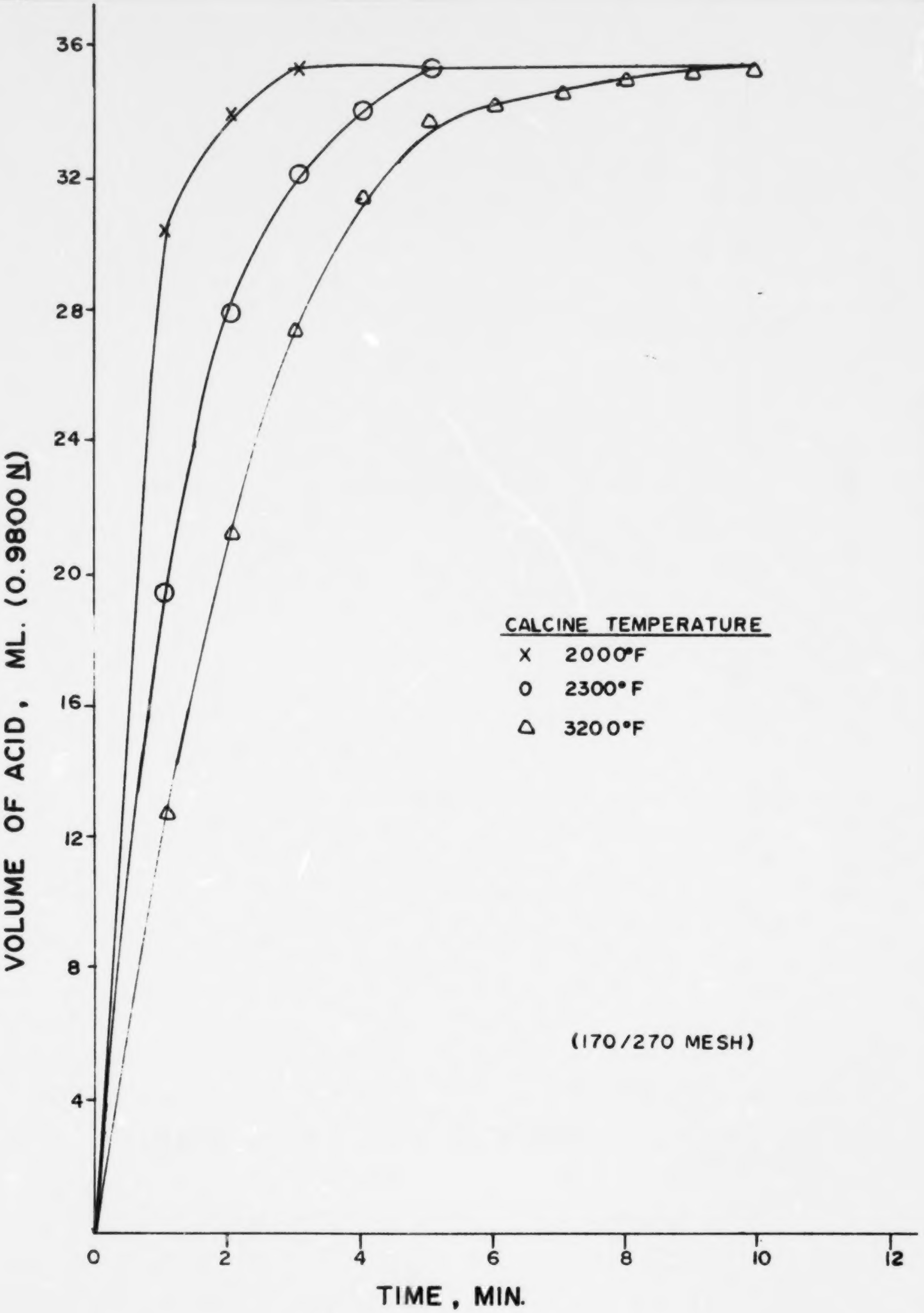


4. Dissolution Rate VS Temperature



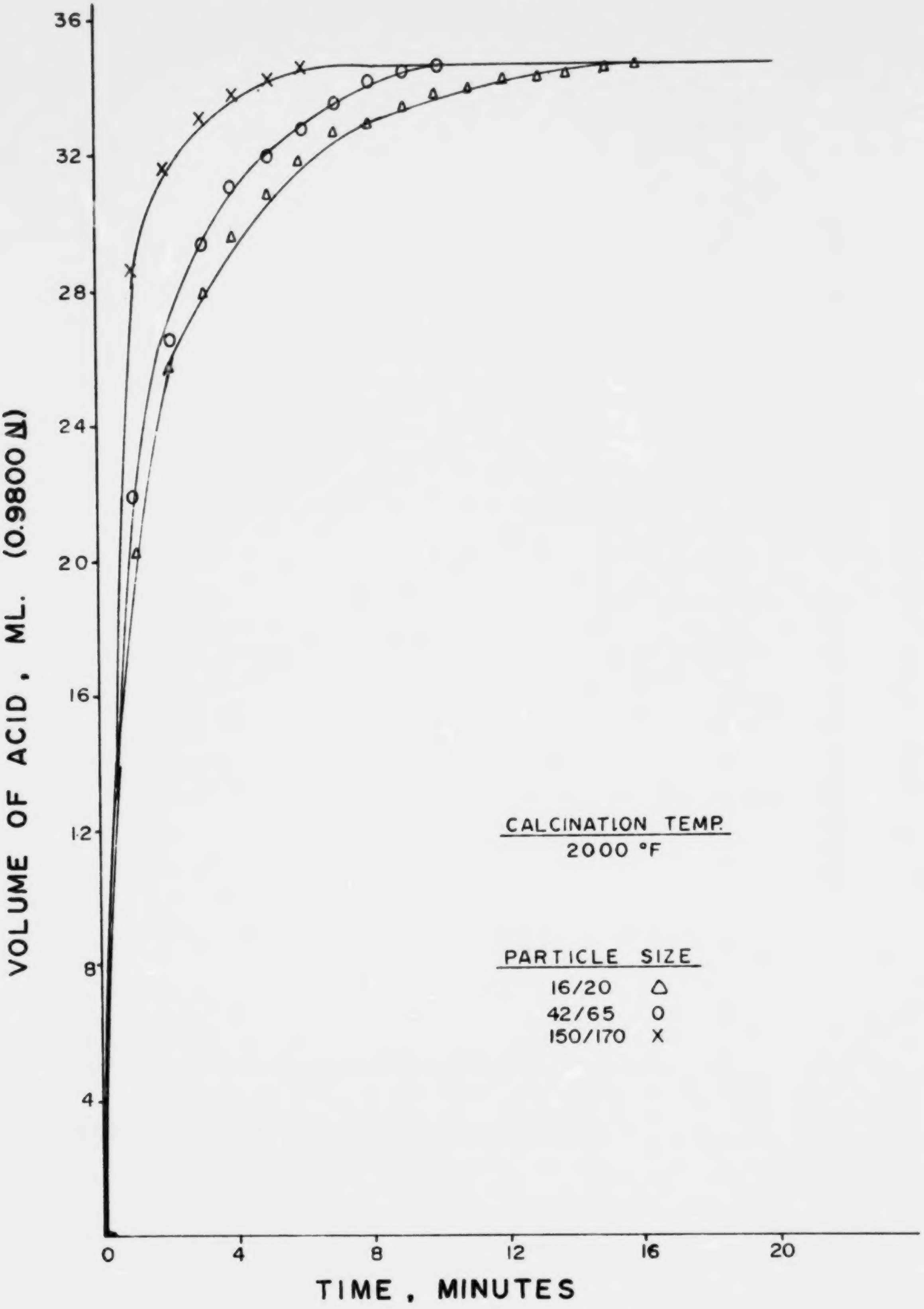


5. Dissolution Rate VS Particle Size

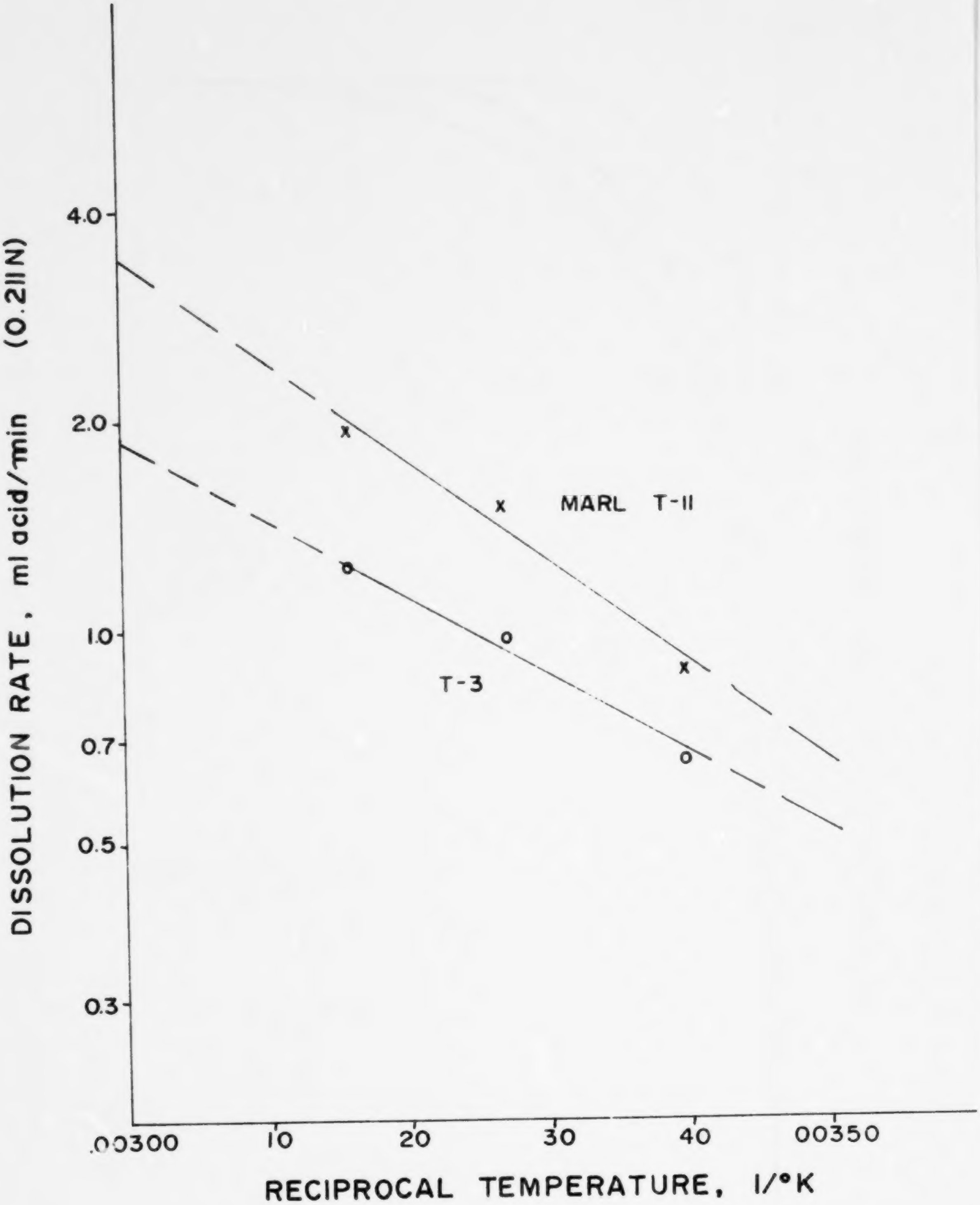


6. Effect of Calcination Temperature on Dissolution

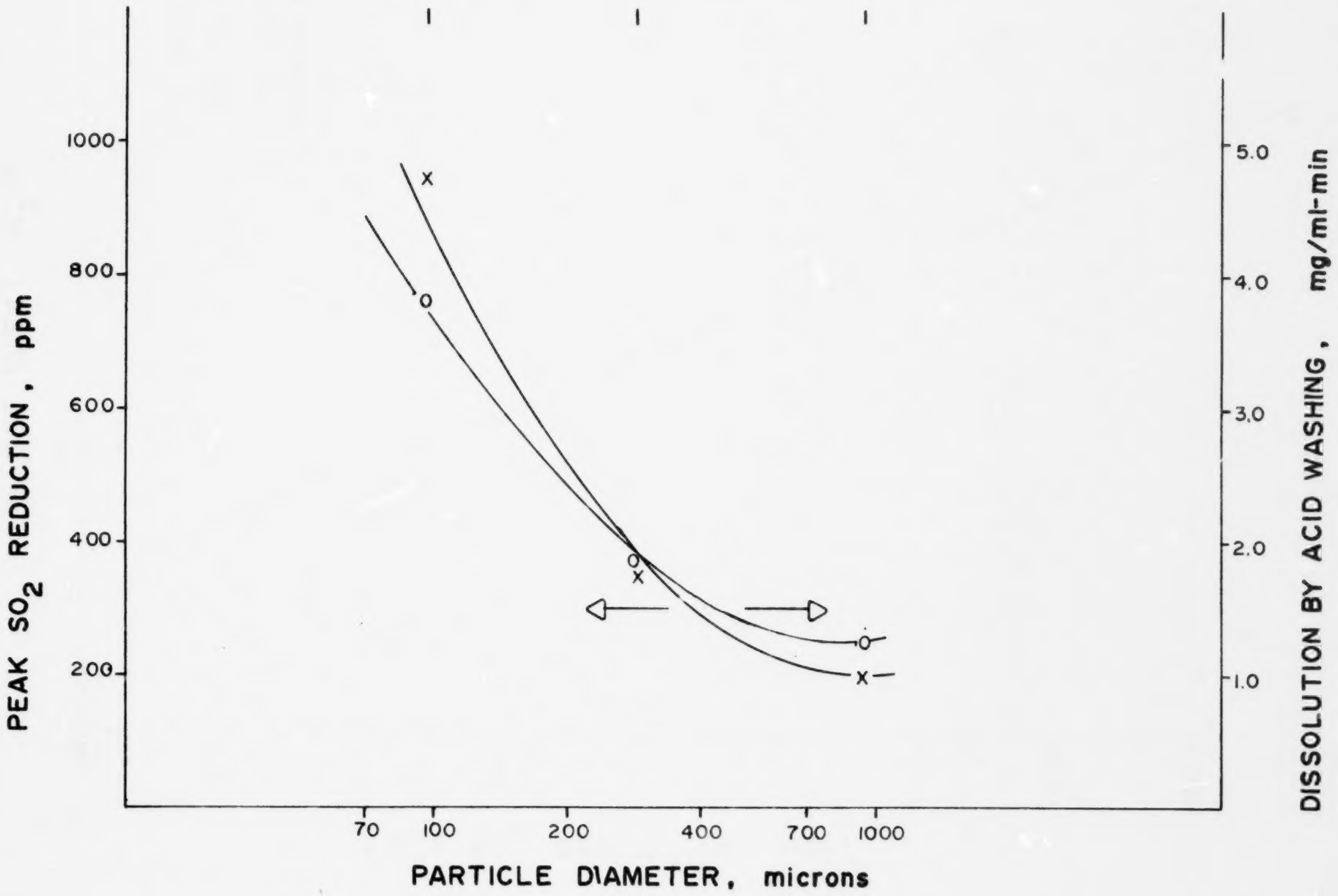
7. Effect of Particle Size



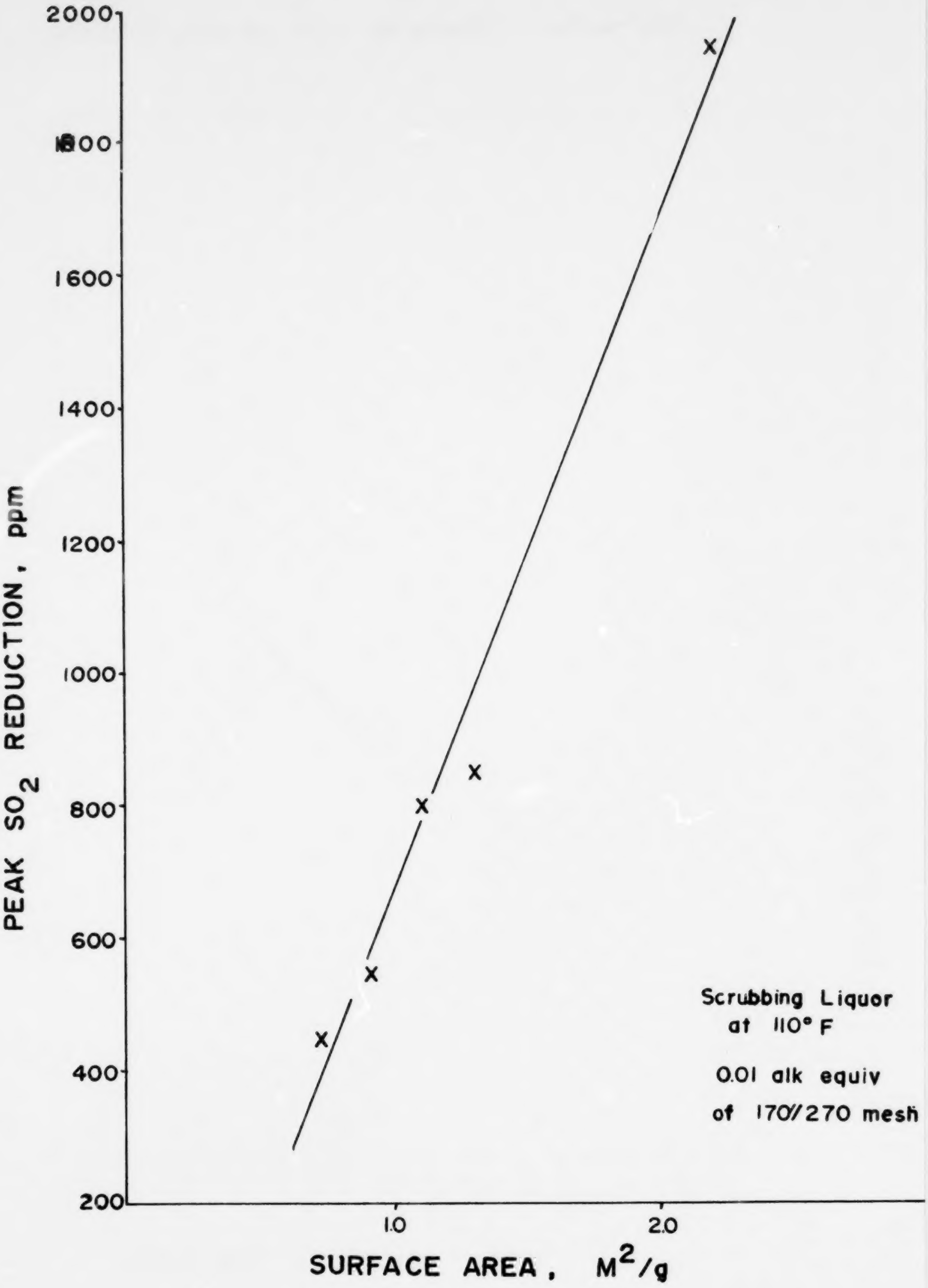
8. Arrhenius Plot of Dissolution Data



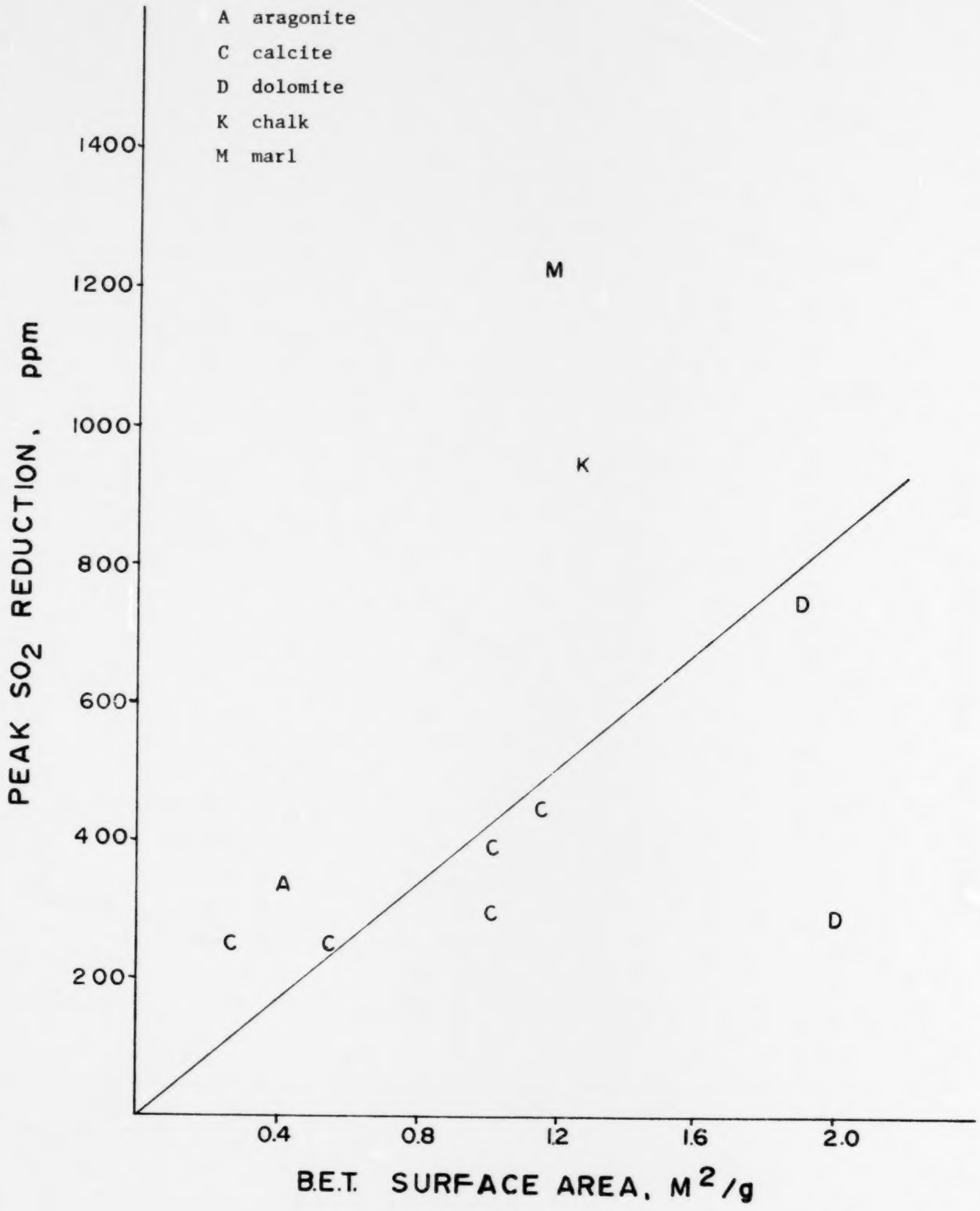
9. Comparison of the Effect of Particle Size on Dissolution and on SO_2 Reduction using Uncalcined Marl



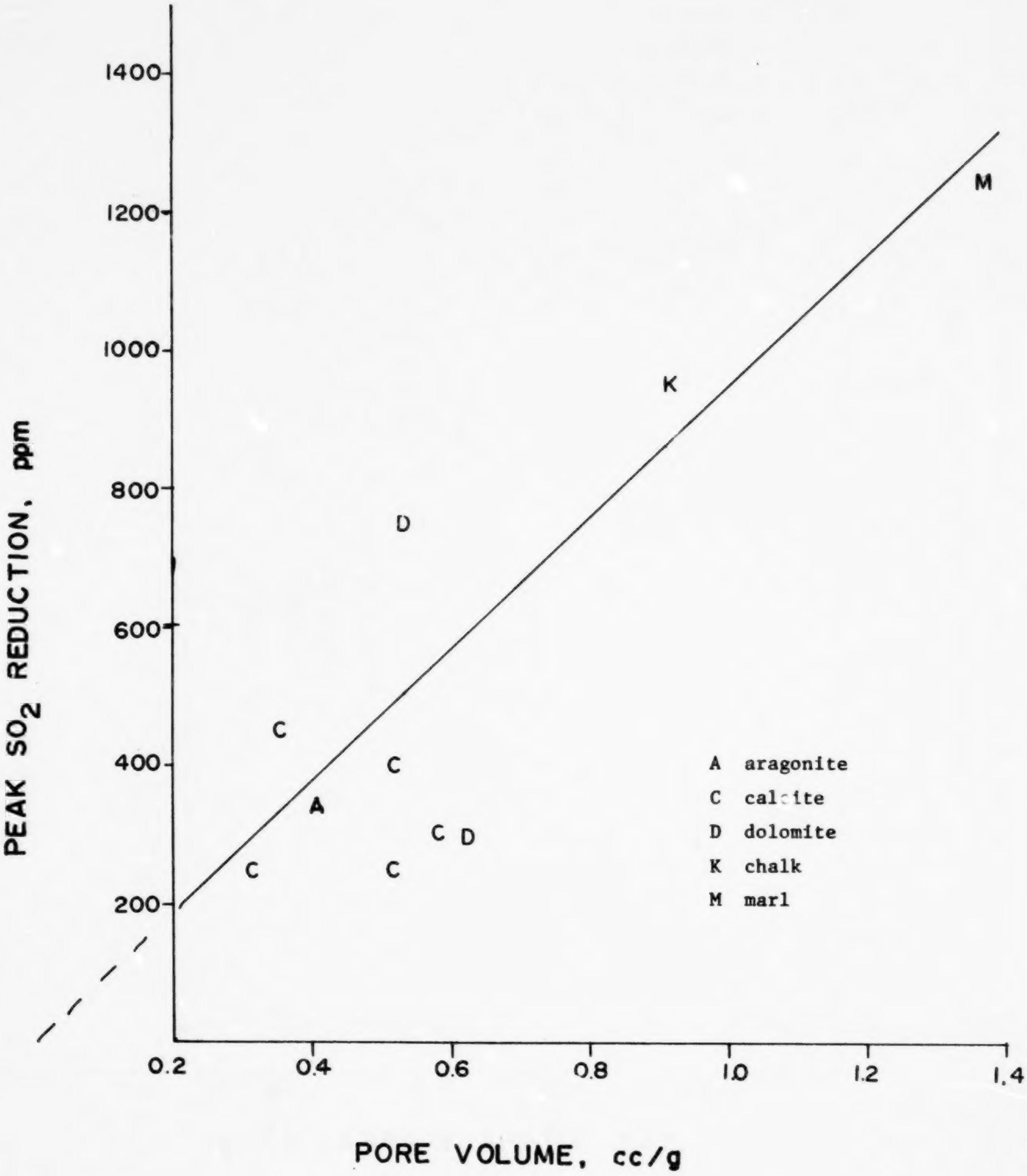
10. Correlation of SO_2 Reduction to Surface Area When Calcination Temperature is Varied



11. Correlation of SO_2 Reduction to Surface Area for Different Calcined Limestone



12. Correlation of SO_2 Reduction to Pore Volume for Different Calcined Limestones



REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY:

SMALL-SCALE STUDIES AT TVA

By

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ABSTRACT

Results from tests with a spray scrubber (two-stage, countercurrent, 4-in. diameter, 4-8 ft^3/min gas flow) are presented. The following parameters were studied.

- Surge tank volume was important; SO_2 removal increased with tank volume up to about 900 gal/(lb SO_2)(min). Apparently the effect was due to providing retention time for completing reactions begun in the scrubber.

- Increase in inlet gas temperature reduced absorption significantly, presumably because of increased SO_2 vapor pressure over the liquor leaving the scrubber.

- High liquor:gas ratio was required for good absorption. The ratios used, on the order of 80 gal/Mcf of gas, were probably higher--because of relative inefficiency of the spray scrubber--than needed in practice. The beneficial effect of high liquor rate indicates the importance of high "effective stoichiometry" (moles $CaCO_3$ to which a mole of SO_2 is exposed during passage through the scrubber).

- Use of excess limestone (beyond stoichiometric) was effective; however, under the scrubber conditions used the stoichiometric amount was adequate (about 90% removal). Under less favorable conditions, excess limestone might have a major beneficial effect by increasing the steady-state effective stoichiometry in the scrubber recirculating loop.

- Increase in inlet SO_2 concentration gave higher exit concentration and slightly lower percentage removal.

- Decrease in limestone particle size improved absorption but not to a major degree.

- Limestone type was not an important variable. Dolomitic limestone was somewhat less effective, but performance of high-calcium limestones was generally similar when particle sizes were comparable.
- Increase in solids content of the slurry improved absorption when other conditions were such as to give relatively low scrubbing efficiency.
- Ionic strength of the scrubber solution was shown to be significant; increase in ionic strength by addition of magnesium sulfate improved absorption.
- Use of an oxidation inhibitor was effective in reducing sulfite oxidation.

Calcium sulfite, the preponderant solid species formed, crystallized in very small platelets that settled slowly and tended to blind limestone surfaces when conditions were such as to limit limestone dissolution rate and thus promote reduction in pH. Oxidation to sulfate was an effective means of avoiding these problems.

In tests of alkali scrubbing followed by regeneration with lime or limestone, alkali bisulfite was easily regenerated to sulfite with limestone. Sulfate purging is still a problem, but if ammonia is used as the alkali the sulfate can be separated and either sold or regenerated with lime.

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY:

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A test program on limestone scrubbing in a small (5-cfm) continuous scrubber has been under way at TVA for about 2 years.[1] The main purpose of the tests has been to support the pilot plant program (2000-3000-cfm scrubber) being carried out at TVA's Colbert Steam Plant, which in turn is aimed at supplying information for design of a full-scale 550-mw installation at TVA's Widows Creek Steam Plant. Much of the work with the small-scale test loop has been concerned with roughing out the effect of variables as a guide for the pilot plant; for this the unit has served the purpose well. However, difficulty in controlling the continuous, loop-type system closely, coupled with the small size of the unit, has made it difficult to obtain precise data. Nevertheless, the data obtained can be used to throw some light on the chemical and kinetic factors involved.

The scrubber loop assembly is shown in Figure 1. Two important changes in operating procedure have been made during the past year. Easier startup and better combustion control have been attained by burning straight natural gas to provide stack gas instead of the previous admixture of gas with oil containing carbon disulfide; sulfur dioxide is fed to the combustion chamber from cylinders to provide about 3000 ppm in the stack gas. Also, commercial spray nozzles are now used instead of the previous impingement type, making it possible to use lower and more conventional liquid:gas ratios.

The stack gas is fed upward through the spray scrubber, which consists of two separate stages each with its own circulating slurry system. Fresh limestone slurry fed to the surge tank for the upper slurry system causes overflow to the lower surge tank. Spent slurry overflows from this tank and is filtered; the filtrate is used in making fresh limestone slurry and the spent solids (wet) are discarded.

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[1] Slack, A. V. "Absorption of Sulfur Dioxide in Limestone Slurry: Small-Scale Tests at TVA." Paper presented at International Symposium on Lime/Limestone Scrubbing for SO_2 Control (sponsored by NAPCA), Pensacola, Florida, March 16-20, 1970.

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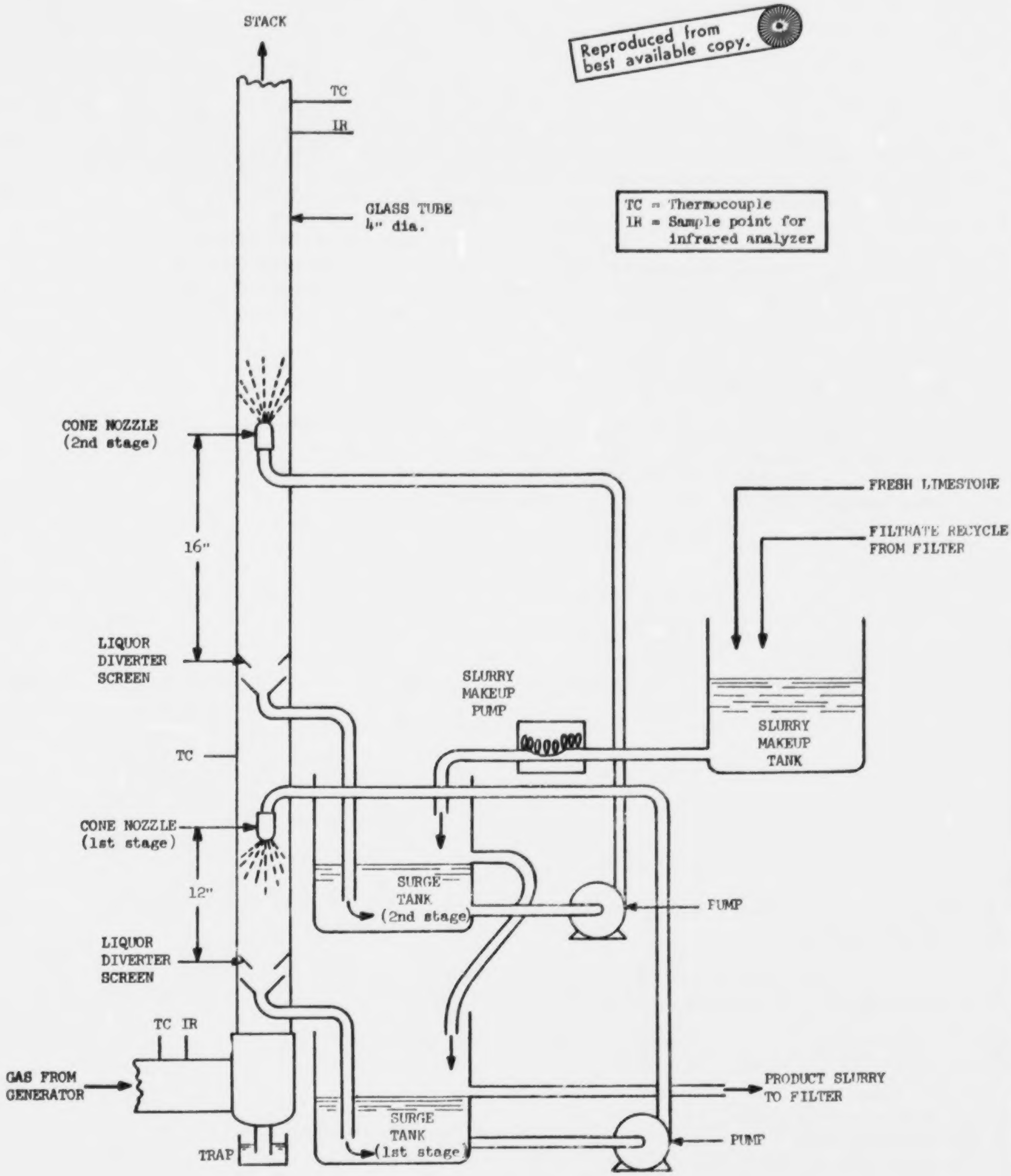


FIGURE 1

Small-Scale Scrubbing System Used in Study of Sulfur Dioxide Removal from Stack Gas by Limestone Slurry Scrubbing

In operation, the unit is started up with the surge tanks full of limestone slurry of the prescribed solids content. The stoichiometry is quite high in the beginning, of course, but the slurry is circulated without limestone makeup until the SO_2 removal has declined to the expected level (from previous experience). The limestone feed is then started. The SO_2 removal adjusts to the test conditions and usually levels out quickly. The scrubbing is then continued until continued uniform SO_2 removal indicates that steady-state operation has been attained. By this means, a datum point at steady state can be obtained in a day's operation.

Absorption Mechanism

Recent work by various investigators has clarified the situation somewhat in regard to the nature and extent of reactions occurring in the scrubber, although there appears to be some disagreement still. There is some support for the following set of reactions:

$$SO_{2(g)} \rightleftarrows SO_{2(aq)} \quad (1)$$

$$SO_{2(aq)} + H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \quad (2)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^= \quad (3)$$

$$CaCO_{3(s)} \rightleftarrows CaCO_{3(aq)} \quad (4)$$

$$CaCO_{3(aq)} \rightleftarrows Ca^{++} + CO_3^= \quad (5)$$

$$Ca^{++} + SO_3^= + 0.5H_2O \rightleftarrows CaSO_3 \cdot 0.5H_2O_{(s)} \quad (6)$$

$$CO_3^= + H^+ \rightleftarrows HCO_3^- \quad (7)$$

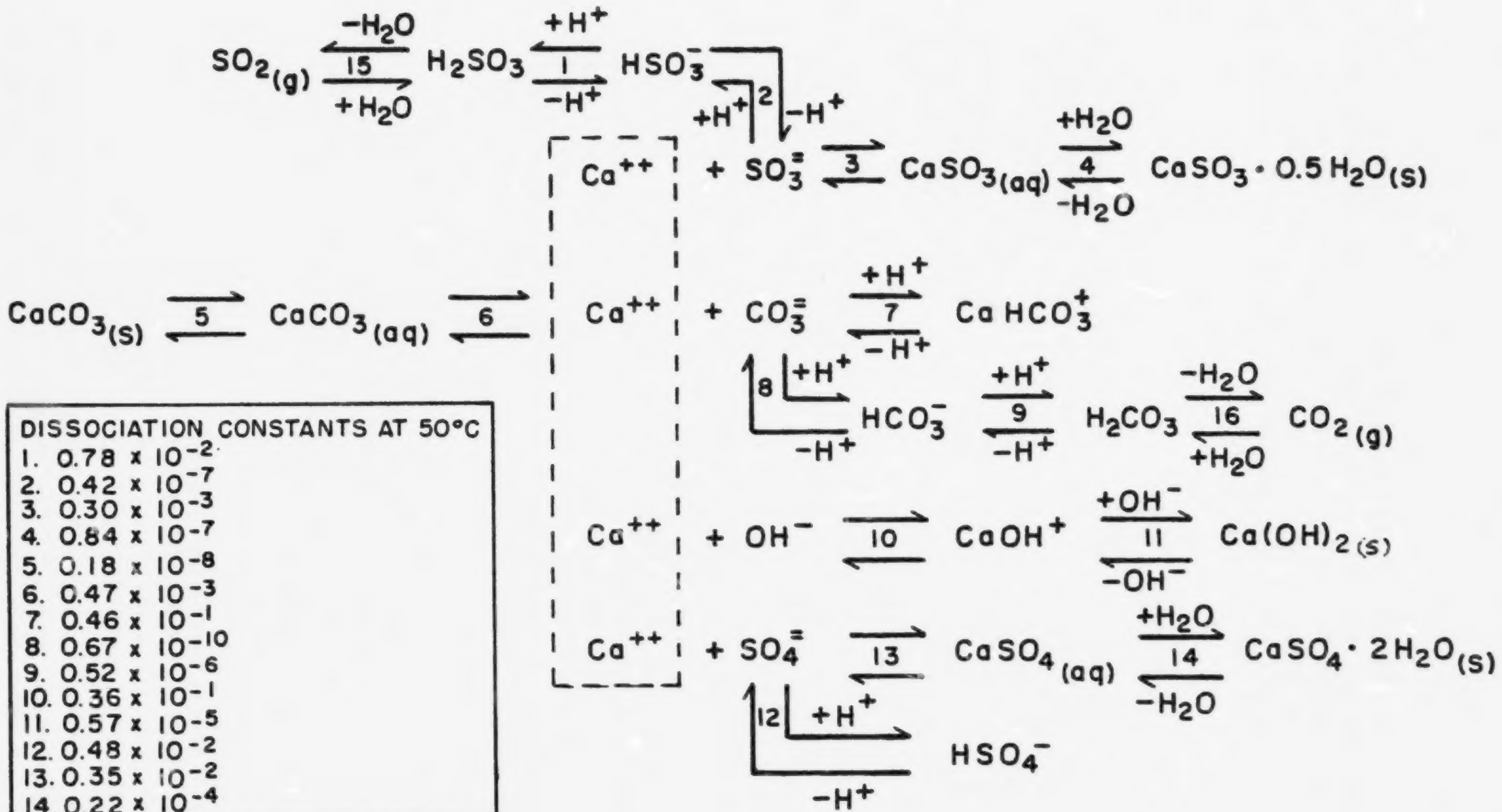
$$H^+ + HCO_3^- \rightleftarrows H_2CO_{3(aq)} \rightleftarrows CO_{2(g)} + H_2O \quad (8)$$

A diagram of the complicated set of relationships involved is given in Figure 2.

For such a set of reactions there are several resistances, both diffusional and chemical, that can affect the rate of the overall reaction:

$$\begin{aligned} &CaCO_{3(s)} + SO_{2(g)} + 0.5H_2O \rightarrow \\ &CaSO_3 \cdot 0.5H_2O_{(s)} + CO_{2(g)} \quad (9) \end{aligned}$$

These include (1) diffusion of SO_2 to and through the gas-liquid film, (2) dissolution of SO_2 and $CaCO_3$, (3) hydrolysis of SO_2, (4) diffusion through the liquid film and into the droplet interior, (5) reaction of H^+ and $CaCO_3$, and (6) reaction of Ca^{++} and $SO_3^=$. Added to these are auxiliary rates such as oxidation rate of dissolved sulfite species and crystallization rate of $CaSO_3 \cdot 0.5H_2O$ and $CaSO_4 \cdot 2H_2O$ (which have a strong tendency to supersaturation.)



DISSOCIATION CONSTANTS AT 50°C
1. 0.78×10^{-2}
2. 0.42×10^{-7}
3. 0.30×10^{-3}
4. 0.84×10^{-7}
5. 0.18×10^{-8}
6. 0.47×10^{-3}
7. 0.46×10^{-1}
8. 0.67×10^{-10}
9. 0.52×10^{-6}
10. 0.36×10^{-1}
11. 0.57×10^{-5}
12. 0.48×10^{-2}
13. 0.35×10^{-2}
14. 0.22×10^{-4}
HENRY'S LAW CONSTANT, 50°C
15. 0.54
16. 0.019

FIGURE 2

Equilibria in the System CaO-SO_2-SO_3-CO_2-H_2O

Added MgO gives similar equilibria, with Mg^{++} replacing Ca^{++}. Added Na_2O and N_2O_5 give the species $CaNO_3^+$, NaOH, $NaCO_3^-$ $NaHCO_3$, $NaSO_4^-$, and $NaNO_3$. Added HCl gives Cl^- ions only.

Work by Boll[1] has indicated that both diffusion and chemical reaction are rate controlling, and that rate of $CaCO_3$ dissolution and of gas phase diffusion are likely to be the important parameters. He also concluded that the chemical reaction is first order with respect both to the limestone surface area per unit of liquid volume and to the SO_2 partial pressure in equilibrium with the liquid.

Distribution of Reactions in Scrubber Loop

There is a further consideration in operation of a countercurrent scrubber, in that pH can drop as the slurry flows down the scrubber and the concentration of dissolved sulfite species can thereby be increased. This not only increases rate of $CaCO_3$ dissolution in the lower part of the scrubber (because the equilibrium partial pressure of SO_2 over the liquid is increased) but also may leave some "free SO_2" in solution that will react with $CaCO_3$ outside the scrubber if given time before return of the slurry to the scrubber.

This is analogous to use of $Mg(OH)_2$ for SO_2 absorption in the paper pulp industry, where all the SO_2 absorbed during a scrubber pass can be kept in solution (no crystallization in scrubber) because of the high solubility of $Mg(HSO_3)_2$ at low pH. The main difference between this and the calcium system is that in the latter the solubilities of the various sulfite species are much lower, so that all the SO_2 absorbed in a scrubber pass (under normal conditions of liquor rate and SO_2 inlet concentration) cannot be held in solution (except perhaps by supersaturation). Therefore part of the absorption in a given pass must be accounted for by crystallization in the scrubber and the remainder by increase of sulfite concentration in the solution. The magnitude of the latter will depend on the pH level at the scrubber exit, which in turn depends on inlet SO_2 partial pressure, liquor flow rate, and type of scrubber (fully countercurrent vs partially backmixed).

Calculated data for the effect of pH on solubility of calcium, sulfite, and sulfate in the system $CaO-SO_2-SO_3-H_2O$ are given in Figure 3. Sulfite solubility increases rapidly with decrease in pH. Therefore the net amount of dissolved sulfur species picked up in the scrubber depends on the net change in pH, which depends on many factors. A calculation was made based on the following assumptions:

pH of inlet slurry	6.0
pH of slurry leaving scrubber	5.0
L/G, gal slurry per Mcf of gas	40
Inlet SO_2 concentration in gas	2500 ppm
Outlet SO_2 concentration in gas	250 ppm

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[1] Boll, R. H. "A Mathematical Model of SO_2 Absorption by Limestone Slurry." Paper presented at International Symposium on Lime/Limestone Scrubbing for SO_2 Control (sponsored by NAPCA), Pensacola, Florida, March 16-20, 1970.

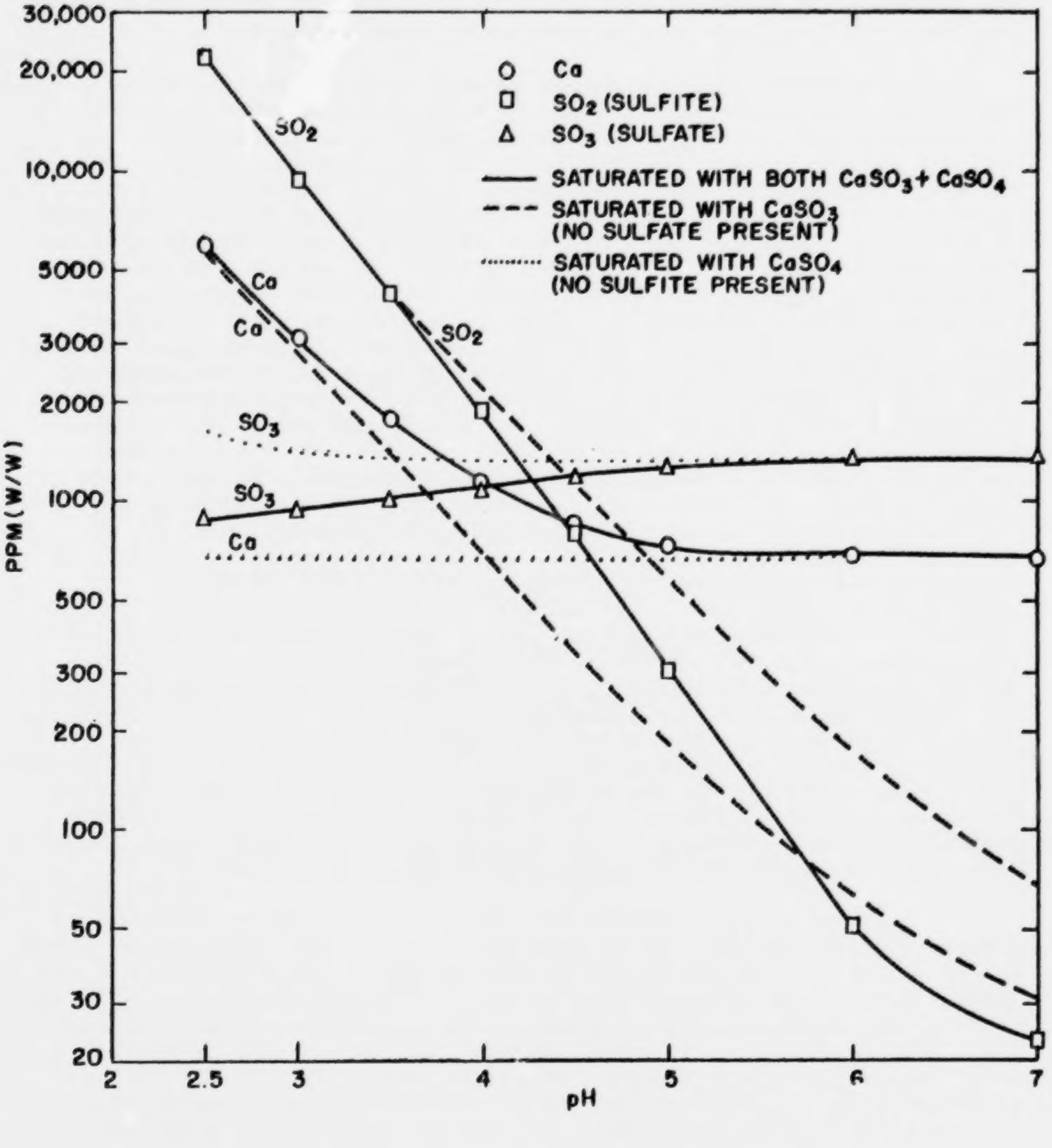

FIGURE 3

Solubility Relationships in the System $CaO-SO_2-SO_3-H_2O$ at 50°C (122°F)

Assuming saturation equilibrium at both scrubber inlet and outlet, about 20% of the total SO_2 absorption can be accounted for by formation of dissolved species, which at the pH involved is mainly bisulfite (HSO_3^-); the remaining 80% can be assumed either to have crystallized in the scrubber as $CaSO_3 \cdot 0.5H_2O$ or to be held in solution by supersaturation.

The assumed decrease of one pH unit (from 6.0 to 5.0) may or may not be close to the actual value. The pH at the scrubber outlet is a transient value, because as soon as the slurry is no longer exposed to the high driving force of the SO_2 and CO_2 in the inlet gas, these gases can start escaping from the liquid phase. Moreover, dissolved sulfite species continue reacting with $CaCO_3$ and therefore raise the pH. The value needed is the instantaneous pH at the point where incoming gas and effluent liquor part company, which is somewhat difficult to measure. In the ICI-Howden work in England,[1] the pH drop in the scrubber was reported to be 0.4 pH unit (from 6.5 to 6.1) for limestone and 0.8 unit (6.9 to 6.1) for lime. In the TVA pilot plant tests with limestone slurry, the pH as measured runs about 6.0 in the feed to the scrubber and about 5.7 in the receiving tank from the scrubber. In the small-scale TVA scrubber, tests were run in which the pH probes were inserted into the scrubber drain line to give a continuous reading, thereby avoiding the possible increase in scrubber outlet pH caused by the delay between sampling and measuring when a grab sample is taken. For an L/G of 88 gal/Mcf, 97% removal of 3200 ppm SO_2, 1.0 limestone stoichiometry, and inlet gas temperature of 150°F, the pH was 6.06 at the scrubber liquor inlet and 5.22 at the outlet. The drop of 0.8 pH unit is close to the 1.0 assumed in the above calculation.

The foregoing does not take into account the possible effect of supersaturation on distribution of crystallization in the scrubber loop. To the extent that calcium sulfite - sulfate forms in the scrubber and does not crystallize because of supersaturation, the crystallization must take place outside the scrubber. Calculated data on relationship between pH, degree of calcium sulfite supersaturation, sulfate:sulfite ratio in solution, and SO_2 vapor pressure for the system CaO-SO_2-SO_3-H_2O are given in Figure 4. These indicate that SO_2 vapor pressure does not increase much with supersaturation; thus a very high degree of supersaturation would be required to interfere with absorption in the pH range normally encountered.

Figure 4 also indicates that under the conditions encountered in limestone scrubbing (pH of about 6 and $SO_4^=$:total S ratio in solution of 0.60 to 0.90), the solution may be highly supersaturated. In the reports of the English work, it is indicated that at the circulation rates necessary to avoid scaling, the supersaturation developed (over saturation concentration) was about 340 ppm each for sulfite and sulfate. At the pH level involved (6.0 to 6.3), this would be a high degree of sulfite saturation. In the TVA work, analyses of the scrubber effluent solution has indicated a considerable supersaturation of both calcium sulfite and sulfate, considerably higher than had been expected. The situation is being explored further.

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[1] Pearson, D. L., Nonhebel, G., and Ulander, P. H. N. J. Inst. Fuel VIII (39), 119-156 (February 1935).

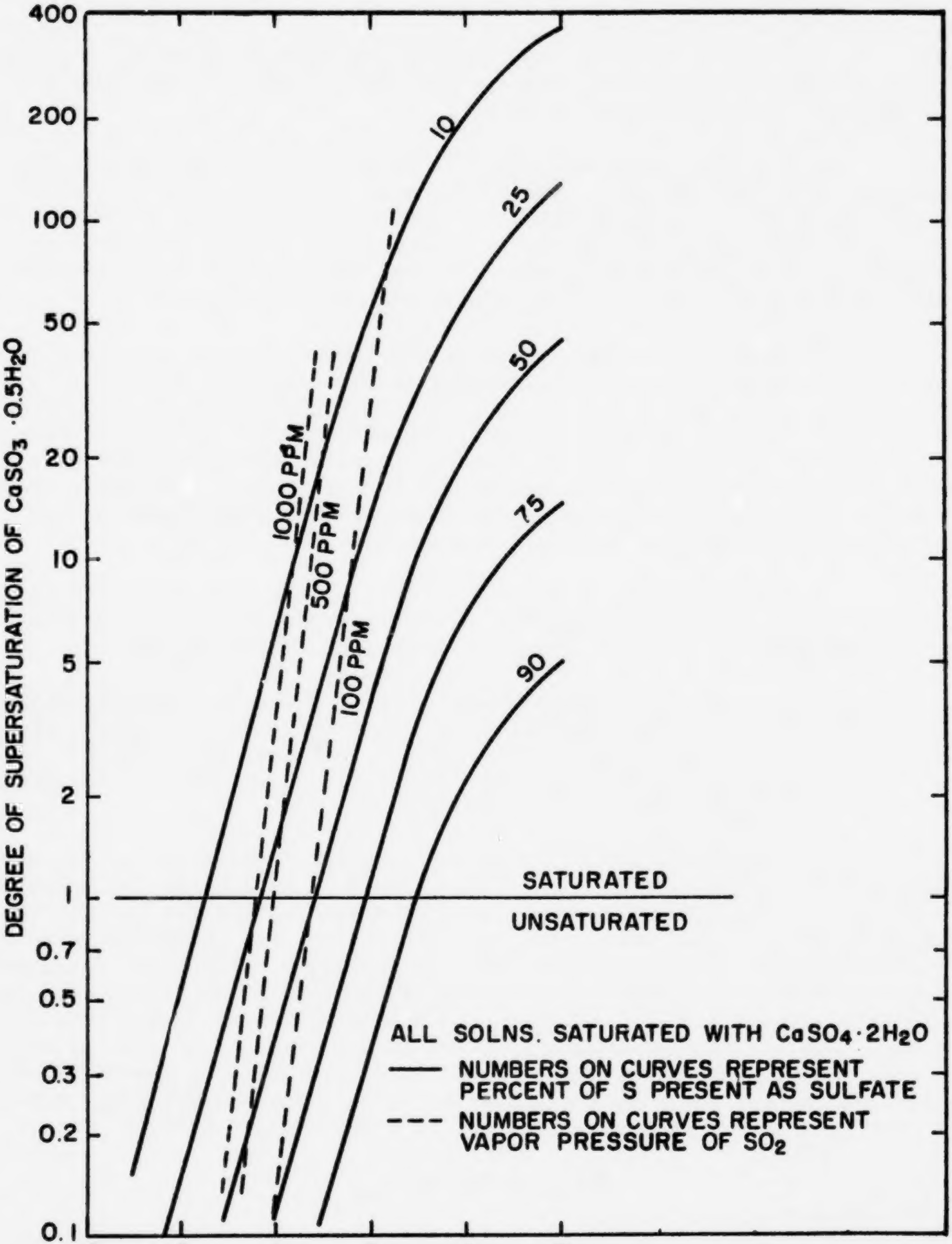

FIGURE 4

Supersaturation of $CaSO_3 \cdot 0.5H_2O$ in System $CaO-SO_2-SO_3-H_2O$

The effect of pH on liquid phase composition, assuming a given degree of supersaturation for calcium sulfite and sulfate, is given in the computer printouts shown in Table I.

Surge Tank Retention Time: In view of the foregoing, it appears that the surge tank in the scrubber loop must serve the functions of (1) completing reactions between limestone and dissolved acidic sulfite species and (2) crystallizing calcium sulfite and calcium sulfate formed in the scrubber but not yet precipitated. The size of this tank and the resulting retention time obviously are important design considerations.

The effect of surge volume on SO_2 removal in the small-scale scrubber is shown in Figure 5. The data indicate a major benefit from increase in surge tank volume up to about 500 gal/Mcfm (or about 1000 gal/lb $SO_2 \cdot$min); further increase had only a small effect. At this surge volume: gas ratio, the retention time in the surge tank at the 37 gal/Mcf rate was about 7 min as compared with 3 min at the 100 gal rate. Presumably the lower reactive sulfite concentration at the higher liquor rate required less time for sufficient limestone to dissolve and react.

A retention time on the order of 2 to 3 min was specified in the ICI-Howden work (about 1000 ppm SO_2 and 115 gal/Mcf) to control scaling. This corresponds to a surge volume of about 1500 gal/lb $SO_2 \cdot$min.

Gas and Solution Temperature: One of the more important variables in the TVA work has been inlet gas temperature (Fig 6). Presumably the adverse effect of high temperature is due to stripping of dissolved sulfite species not yet reacted with calcium, thus reducing the amount of reaction that can be accomplished in the surge tank.

The magnitude of the effect appears too large even for the maximum amount of unreacted sulfite species that could be present in the solution (on the basis of calculated values). A possible explanation is that the high temperature heats the liquid film on droplets and thus interferes with gas-liquid transfer. In other words, the stripping may not involve dissolved equilibrium species, which would require both heating the entire drop and also a relatively low pH in the drop to develop any significant back pressure of SO_2. Instead, the dissolution of SO_2 in the liquid film and the hydrolysis to H_2SO_3 may be inhibited, which would reduce not only the amount of dissolved unreacted species but also the supply of sulfite for the $Ca^{++}/SO_3^{=}$ reaction in that part of the scrubber affected. For the equilibrium

$$SO_{2(g)} \rightleftarrows SO_2 \cdot H_2O_{(aq)} \qquad (10)$$

The effect of temperature on the Henry's law constant ($h = a_{SO_2 \cdot H_2O}/P_{SO_2}$) is as follows:

TABLE I

Effect of pH on Liquid Phase Compound at Given Degrees of Sulfite and Sulfate Supersaturation[a]

```
PH=   5.0       S1=  4,0       S2= 1,56       PCO2= 0,0067

SPECIES    ACTIVITY     MOLALITY    ACT,COEFF

  H2O                                0.99917
    H   0,1000E-04   0,1195E-04   0,8367E+00
   OH   0,5477E-08   0,6900E-08   0,7938E+00
H2SO3   0,1302E-04   0,1286E-04   0,1012E+01
 HSO3   0,1019E-01   0,1285E-01   0,7926E+00
  SO3   0,4341E-04   0,1100E-03   0,3947E+00
CASO3   0,1136E-02   0,1122E-02   0,1012E+01
   CA   0,7741E-02   0,1895E-01   0,4084E-00
 CAOH   0,1102E-08   0,1409E-08   0,7936E+00
CAHCO3  0,1086E-05   0,1370E-05   0,7938E+00
CACO3   0,7100E-09   0,7015E-09   0,1012E+01
CASO4   0,9753E-02   0,9635E-02   0,1012E-01
 HSO4   0,9193E-05   0,1158E-04   0,7938E+00
  SO4   0,4448E-02   0,1241E-01   0,3583E+00
H2CO3   0,1252E-03   0,1252E-03   0,1000E+01
 HCO3   0,6453E-05   0,8142E-05   0,7926E+00
  CO3   0,4350E-10   0,1102E-09   0,3947E+00


                                  DISTRIBUTION, %
    CALCIUM           SULFITE            SULFATE              CO2
CASO3    3.8       H2SO3    0.1       CASO4  43.7       CAHCO3    1.0
   CA   63.8        HSO3   91,2        HSO4   0,1        CACO3    0,0
 CAOH    0,0         SO3    0,8         SO4  56,3        H2CO3   92,9
CAHCO3   0.0       CASO3    8,0                           HCO3    6,0
CACO3    0,0                                               CO3    0,0
CASO4   32,4


PH=   6,0       S1=  4,0       S2= 1,56       PCO2= 0,0067

SPECIES    ACTIVITY     MOLALITY    ACT,COEFF

  H2O                                0,99939
    H   0.1000E-05.  0.1188E-05   0,8417E+00
   OH   0.5478E-07   0,6818E-07   0,8034E+00
H2SO3   0,1570E-06   0.1554E-06   0,1010E+01
 HSO3   0,1229E-02   0,1531E-02   0,8031E+00
  SO3   0,5237E-04   0,1259E-03   0,4159E+00
CASO3   0,1136E-02   0.1124E-02   0.1010E+01
   CA   0,6416E-02   0.1498E-01   0,4282E+00
 CAOH   0,9796E-08   0.1219E-07   0,8034E+00
CAHCO3  0,9015E-05   0.1122E-04   0,8034E+00
CACO3   0,5885E-07   0,5824E-07   0,1010E+01
CASO4   0,9753E-02   0,9652E-02   0,1010E+01
 HSO4   0,1109E-05   0.1381E-05   0,8034E+00
  SO4   0,5367E-02   0.1406E-01   0.3818E+00
H2CO3   0,1252E-03   0.1252E-03   0,1000E+01
 HCO3   0,6453E-04   0.8036E-04   0,8031E+00
  CO3   0,4350E-08   0.1046E-07   0,4159E+00

                                  DISTRIBUTION, %
    CALCIUM           SULFITE            SULFATE              CO2
CASO3    4.4       H2SO3    0.0       CASO4  40.7       CAHCO3    5.2
   CA   58.1        HSO3   55.0        HSO4   0.0        CACO3    0.0
 CAOH    0.0         SO3    4.5         SO4  59.3        H2CO3   57.7
CAHCO3   0.0       CASO3   40.4                           HCO3   37.1
CACO3    0.0                                               CO3    0.0
CASO4   37.5
```

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[a] Degree of supersaturation: for sulfite, 4.0 times saturation; for sulfate, 1.56.

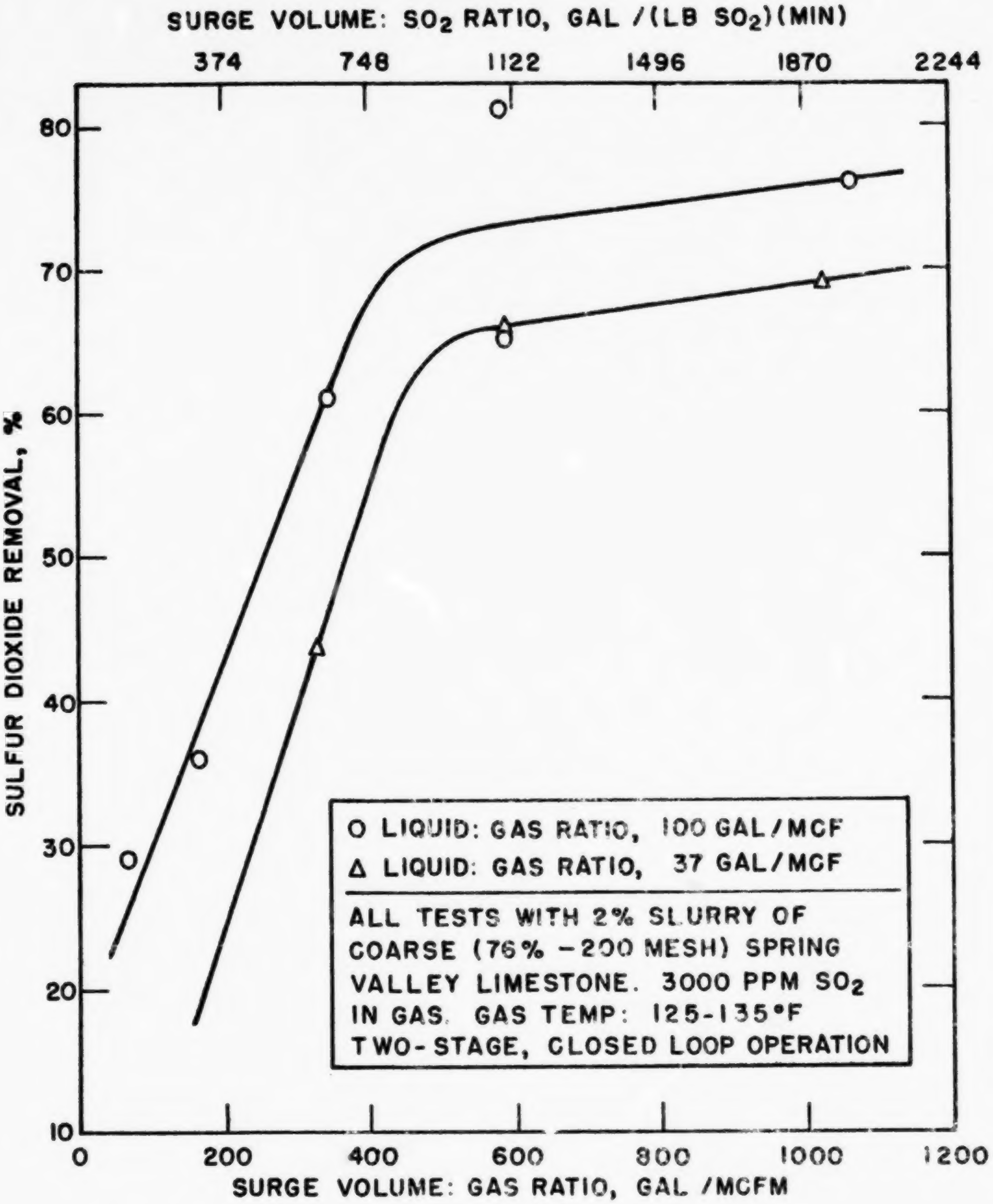

FIGURE 5

Limestone Slurry Scrubbing of SO_2 from Simulated Stack Gas--

Effect of Surge Volume on SO_2 Removal

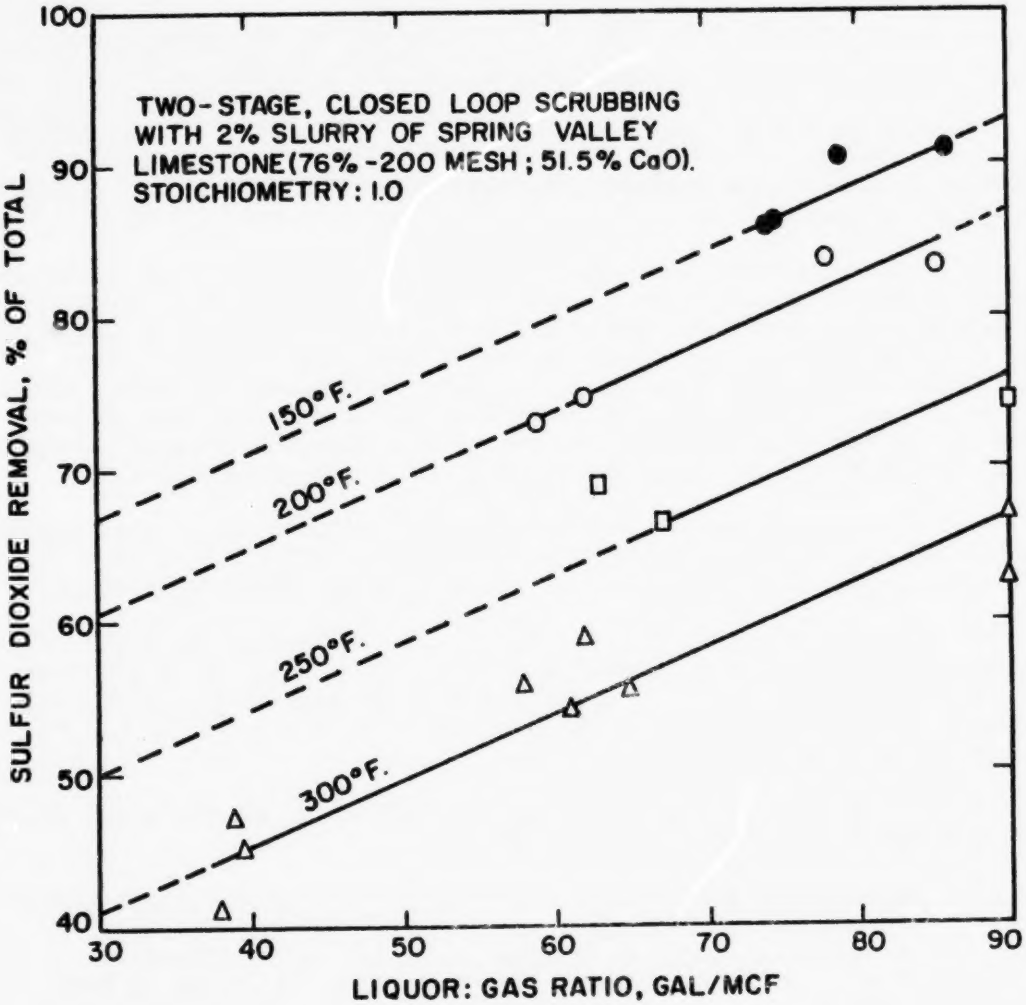

FIGURE 6

Limestone Slurry Scrubbing of SO_2 from Simulated Stack Gas--

Effect of Liquor:Gas Ratio and Inlet Gas Temperature on SO_2 Removal

Temperature, °F	h
150	0.343
200	0.169
250	0.092
300	0.055

At the point of initial gas-liquid contact, the low pH in the liquid film increases the SO_2 back pressure and the increase in film temperature decreases the Henry's law constant, thus reducing transfer through the film and into the droplet.

The effect of inlet gas temperature may not be as significant in pilot or full-scale scrubbers as in the small-scale unit. Presumably the stripping effect of the hot gas would be limited to only a small portion of the scrubber height, since mass transfer of water vapor and consequent cooling of the gas is rapid. Since the height of the small-scale scrubber was quite small as compared with pilot and full-scale sizes, the portion affected by the hot gas would represent a much greater percentage of the total height in the small-scale unit as compared with larger ones.

Tests were run also in which the overall solution temperature was varied and the inlet gas temperature held at 150-200°F (Fig 7). The adverse effect of higher solution temperature on removal was quite significant.

It has been generally considered that large-scale scrubbers would be operated at the wet bulb temperature of the gas, which is on the order of 120-125°F in power plants. However, there may be special situations in which the wet bulb temperature would be higher or lower; the data in Figure 7 indicate the likely result.

Sulfite Oxidation: The degree of sulfite oxidation in and outside the scrubber is important in several ways.

1. Degree of oxidation in the scrubber affects the degree of calcium sulfate supersaturation in the effluent liquid phase, which is an important factor in scaling (see paper in this symposium: "Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Operational Aspects of the Scaling Problem" by A. V. Slack and J. D. Hatfield). There should be no other effect on solution composition, however, as the presence of excess sulfite and sulfate crystals should keep the solution at least saturated at all times (as compared with oxidation of dissolved sulfite in a crystal-free slurry, in which case the sulfite content could drop below saturation and thus affect pH and species distribution).

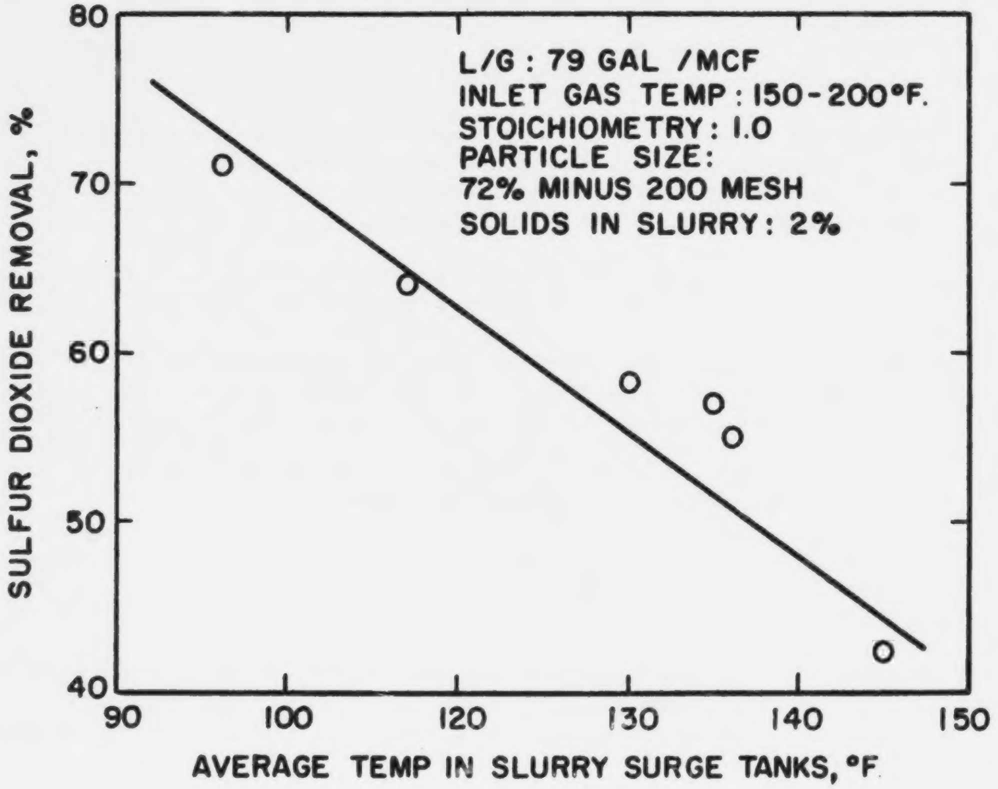

FIGURE 7

Limestone Slurry Scrubbing of SO_2 from Simulated Stack Gas:

Effect of Slurry Temperature

2. There is some evidence that under upset scrubber conditions which promote low pH, the increased sulfite concentration in solution resulting from the low pH causes sulfite crystallization on limestone surfaces and consequent blinding. Increase in oxidation rate would reduce the sulfite content, which perhaps would decrease the blinding effect.

3. Degree of oxidation both in and out of the scrubber affects the sulfate:sulfite ratio in the solid phase, which is important in solids settling because the sulfate crystals grow larger and thus settle better (Fig 8).

4. Oxidation throughout the system, including the waste pond, reduces the possibility of water pollution by sulfite.

5. If a recovery process were operated with $CaO-CaCO_3$ as the absorbent, oxidation would not be desirable because difficulty in decomposing sulfate (as compared with thermal decomposition of sulfite to give a rich stream of SO_2 and to regenerate CaO for recycling) would likely make it better to discard the sulfate and replace it with makeup limestone.

Data on degree of oxidation in the small-scale tests have been somewhat erratic, ranging from 25 to 100% depending on type of spray nozzle and other factors; with the present atomizing nozzles, the range is 70 to 100%. The tests are not applicable to the actual power plant situation anyway, because of the absence of fly ash (which may or may not promote oxidation), absence of phenolic impurities in the gas (which are known to inhibit oxidation), and possible differences in NO_2 content (which is known to promote oxidation).

Data on the composition of solids from pilot plant runs are given in Table II.

The calculated species composition for run B is given in Table III.

There was no opportunity in these runs to study the effect of operating variables on oxidation. Work reported in the literature indicates the following general relationship for sulfite oxidation,

$$- \frac{d(SO_2)}{dt} = \frac{g[HSO_3^-]}{[H]^{1/2}} \qquad (11)$$

where the lefthand term is rate of sulfite oxidation, the term g includes the effects of free radicals and other effects characteristic of the system under study, and [H] is the activity of the hydrogen ion. Thus a decrease in pH may or may not reduce oxidation, depending on how rapidly the HSO_3^- concentration increases as the pH is reduced. In the limestone system,

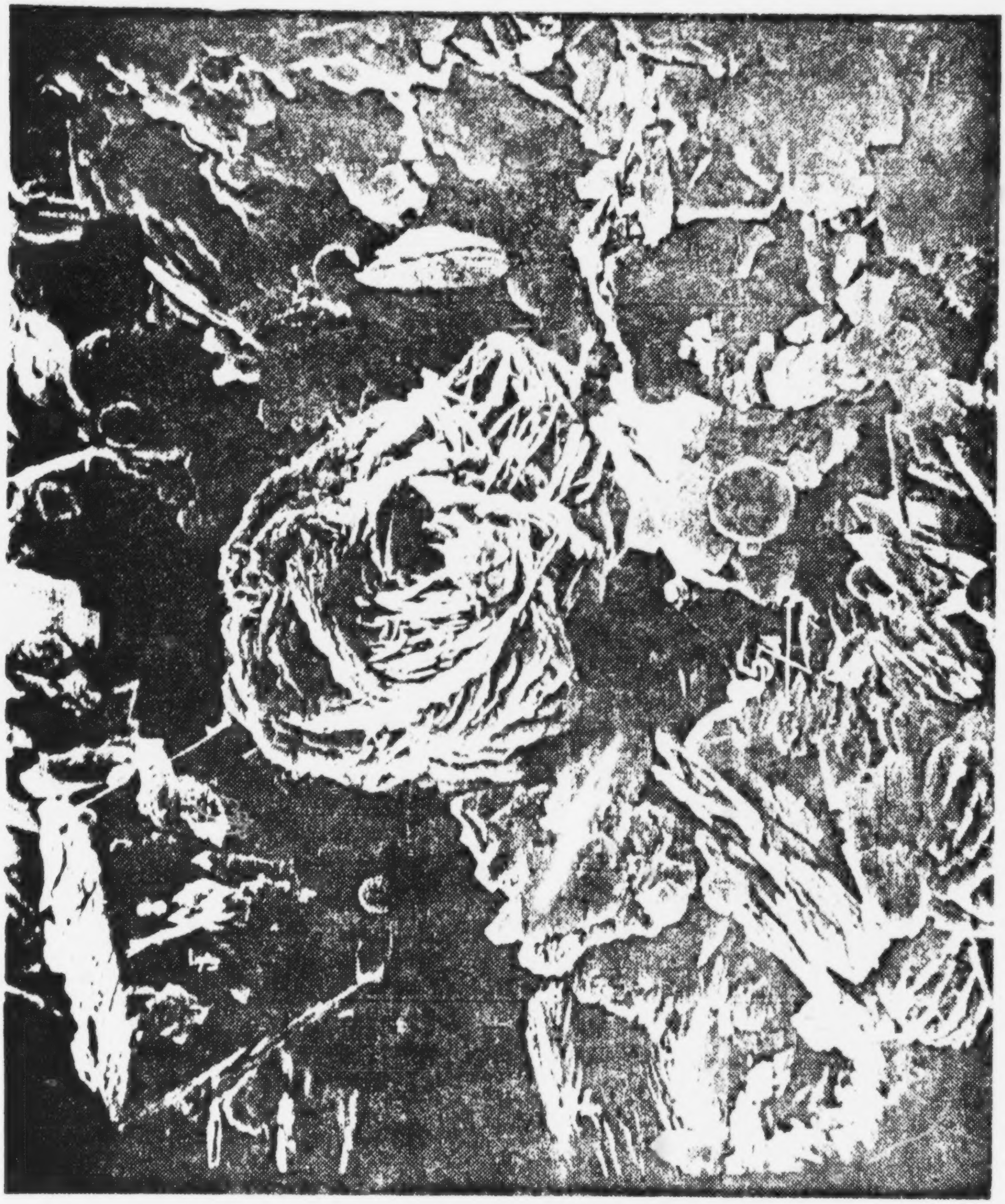

FIGURE 8

Electron Micrograph of Solids Taken from Limestone Scrubber Slurry

The large blocky crystal in the upper lefthand corner is $CaSO_4 \cdot 2H_2O$, the small spheres are fly ash, and the flat platelets are $CaSO_3 \cdot 0.5H_2O$. Some limestone is also present. The rosette in the center is made up of calcium sulfite crystals. (Photograph from work by Dr. G. H. McClellan, TVA.)

a drop in pH from 6.0 to 5.0, in solutions saturated with $CaSO_3 \cdot 0.5H_2O$, increases the value of the $[HSO_3^-]/[H]^{1/2}$ term from 2.10 to 2.35, indicating that pH reduction in this range promotes oxidation. The effect of pH on the term under various conditions of saturation is given in Table IV. The data indicate that pH increase inhibits oxidation except when the solution is saturated with both calcium and sulfite.

TABLE II

Composition of Solid Phase from Pilot Plant Limestone Slurry Tests[a]

Constituent	Weight percent in various runs A	B	C
Ca	24.8	26.6	23.5
Mg	1.0	0.8	0.8
Total S	11.7	10.1	8.0
S as sulfite	9.8	8.2	6.8
S as sulfate[b]	1.9	1.9	1.2
Degree of oxidation, %	16	19	15

---

[a] Limestone composition, %: CaO, 52.3; MgO, 1.2. SO_2 in inlet gas, 2800 ppm. L/G = 60 gal/Mcf. Solids content of slurry: 15-20%.

[b] By difference.

TABLE III

Species Distribution in Solid Phase from Limestone Slurry Scrubbing[a]

Species	Weight percent
$CaSO_3 \cdot 0.5H_2O$	33.0
$CaMg(CO_3)_2$	6.2
$CaSO_4 \cdot 2H_2O$	10.2
$CaCO_3$	31.5
Fly ash	19.0

---

[a] Stoichiometry: 1.5. SO_2 removal, about 65%.

TABLE IV

Effect of pH on $[HSO_3^-]/[H^+]^{1/2}$ in System CaO-SO₂·H₂O

pH	At constant Ca moles/kg H_2O Ca (total)	 SO_2 (total)	Saturation	$[HSO_3^-]/[H^+]^{1/2}$
6.0	0.001525	0.002649	1.00	2.096
5.0	0.001525	0.003005	0.15	0.864
4.0	0.001525	0.003188	0.017	0.291
		At constant SO_2 (total sulfite)		
6.0	0.001525	0.002649	1.00	2.096
5.0	0.001342	0.002649	0.12	0.766
4.0	0.001258	0.002649	0.012	0.244
		At constant saturation		
6.0	0.001525	0.002649	1.00	2.096
5.0	0.004520	0.008725	1.00	2.353
4.0	0.01664	0.03342	1.00	2.670

The preceding discussion refers only to oxidation rate in solution assuming that oxygen is already present. The rate of oxygen absorption should also be important in determining overall rate in a limestone slurry scrubber. Chertkov[1] proposed a generalized empirical equation for oxygen absorption based on data from several scrubbers and differing absorbents.

$$G_o = \frac{0.8Q^{0.7}\cdot a\cdot(S/C)^6}{\gamma\cdot\mu} \qquad (12)$$

where G_o = g O_2 absorbed per hour per m² of liquid/gas contact surface (considered to be equivalent to rate of oxidation)

Q = liquid flow rate, $m^3/m^2\cdot hr$

a = $\frac{t}{50}$, where t is the average solution temperature in °C

S/C = mole ratio of sulfite to absorbing species in solution

γ = solution density, kg/m^3

μ = solution viscosity, $kg\cdot sec/m^2$

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[1] Chertkov, B. A. J. Appl. Chem. USSR 34 (4), 743-47 (1961).

The data currently available from TVA work are not sufficient to evaluate this equation. However, Q is the only variable that can be changed easily, and the minimum level of Q is set by the SO_2 removal requirement.

Another factor is the ratio of O_2 and SO_2 partial pressures in the gas phase, which affects the overall oxidation rate by changing the amount of O_2 absorbed per unit of SO_2. Thus a relatively low SO_2 content in the gas should give relatively high oxidation rate. Comparison of current pilot plant tests on gas from western coal (400-600 ppm)--plus results from the ICI-Howden work (1000 ppm)--with the TVA tests (2500-3000 ppm) indicate that this is true.

The situation in regard to the various promoters involved (fly ash, NO_2, limestone constituents) and inhibitors (phenolics) is somewhat confused. More work must be done before the relative importance of these factors can be determined.

The effect of added inhibitors was tested in the small-scale TVA work. Under conditions that gave 50% oxidation of the solids, the oxidation was reduced to 1% by addition of 0.1% hydroquinone. At the lower pH level resulting from use of benzoic acid to promote SO_2 removal, use of the same amount of hydroquinone reduced oxidation from 95 to 20%. Presumably the larger amount of sulfite available in solution for oxidation at the lower pH increased the percentage oxidation of the solids--both with and without inhibitor. This assumes that oxidation involves the steps of sulfite dissolution, oxidation of sulfite in solution, and crystallization of sulfate. The higher solubility at low pH is taken into account in Table IV.

The discussion thus far has been concerned with oxidation in the scrubber, which may or may not be practicable to change in actual operation. It should be feasible to oxidize outside the scrubber, however, if oxidation is indicated as a means of coping with settling, blinding, and pollution problems. This could be done by passing air or oxygen through the slurry, either through the recycled slurry or through the sidestream diverted for solids separation.

The problem is getting an adequate rate of oxygen absorption in the slurry, which in Japan has led to development of a special "spinning cup" technique to increase absorption. This could be used, or the operation could be carried out under pressure, or both.

Exploratory tests with the spinning cup oxidizer have been made in the TVA small-scale work. Oxidation was much faster than with introduction of the air through fritted glass into a stirred solution; about four times as much air throughput was required with the fritted glass to accomplish complete oxidation. Activated charcoal and titanium increased the rate somewhat but not significantly. Use of ultrasonic energy was not effective.

In the pilot plant, one exploratory test was made in which air was bled into the scrubber (air:gas volume ratio about 1:1) to increase oxidation rate. Oxidation was increased by a major degree, as indicated by increase in calcium sulfate content of the slurry solids.

An oxidizing tower has been installed in the pilot plant and will be tested on the solids-separation sidestream when time is available.

Tests have also been made to determine whether sulfite will oxidize on standing in the waste pond. Samples of moist product slurry solids were stored in 1-in. vertical tubes, unstoppered but taped to prevent exposure to light. No oxidation occurred in storage over a period of 16 weeks.

Surface Area Holdup in Scrubber

Since rate of limestone dissolution appears to be a controlling factor in SO_2 absorption, it is important to have a large limestone surface area per volume of slurry and to hold this area in contact with the gas in the scrubber as long as possible. Hence the requirement can be expressed as surface area of limestone exposed to each unit of SO_2 passed through the scrubber. There are several variables that affect this.

Solids Content of Slurry: A simplified flowsheet for the scrubber loop is shown in Figure 9. A large body of crystals, mainly $CaCO_3$ and $CaSO_3 \cdot 0.5H_2O$ (plus smaller amounts of $CaSO_4 \cdot 2H_2O$, $CaMg(CO_3)_2$, and fly ash), circulate around the loop, to which is added a relatively small stream of $CaCO_3$ and from which is withdrawn a relatively small stream made up of calcium sulfite, unreacted calcium carbonate, and the other solid constituents. Thus the gas is exposed to an amount of limestone in the recycling solids that can be much larger (per unit of SO_2) than the amount of limestone fed. The concentration of limestone in the recycling slurry therefore is an important variable, with a linear effect on the "effective surface area" (limestone surface area in scrubber per unit of SO_2 per unit of time).

Only limited data on effect of solids content in the slurry have been obtained in the small-scale tests; examples are given in Table V. The improvement from increasing solids concentration under conditions that gave a low level of SO_2 removal (single-stage test) was much larger than for those that gave a fairly high level (two-stage). This has been generally true for all variables; more benefit was realized, even on the basis of percentage reduction of unremoved SO_2, when there was more room for improvement.

The increase in limestone surface area per volume of slurry at steady state brought about by doubling the solids content of the slurry should have been about 35% for the one-stage tests and 75% for the two-stage.

In the pilot plant, a much higher solids content is used (12-15%) than is feasible for the nozzles in the small-scale spray tower. The high level is used mainly to provide sulfite-sulfate crystals for scaling control, but some improvement in SO_2 removal has been noted also.

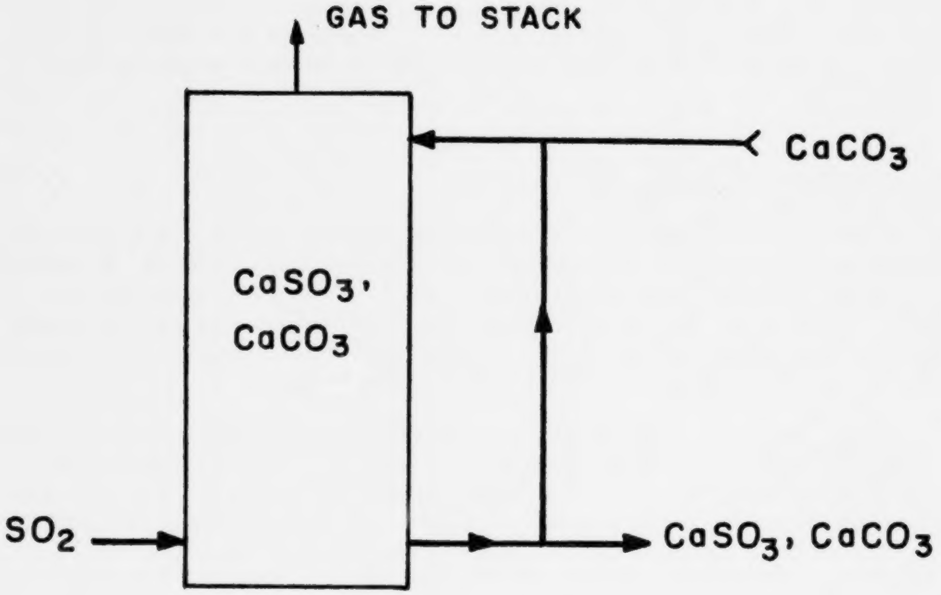

FIGURE 9

Simplified Flowsheet for Limestone Scrubber Loop

Particle Size: The limestone surface area is inversely proportional to the diameter of the particles; for example, breaking 200-mesh particles (74μ) into 325-mesh particles (44μ) should increase surface area by about 70%.

An example of the effect of particle size on SO_2 removal is given in Table VI. Some improvement resulted from finer grinding but the effect was not a major one.

Stoichiometry: Feeding of excess limestone beyond the stoichiometric amount should have a considerable effect on limestone content of the slurry in the circulating loop at steady state. For a stoichiometry of 1.0 and SO_2 removal of 80%, 20% of the calcium (molar basis) in the loop, at steady state, should be in the form of unreacted $CaCO_3$. For 1.2 stoichiometry, assuming the same removal, 33% should be $CaCO_3$. Thus a 20% increase in external stoichiometry gives a 33% increase in "internal" stoichiometry.

TABLE V

Effect of Limestone Slurry Concentration on SO_2 Removal

Slurry concentration, %	SO_2 removal,[a] %
One-stage, L/G = 37	
1	38
2	59
Two-stage, L/G = 72[b]	
1	75
2	78
5	79

---

[a] Feed stoichiometry: 1.0. Closed-loop operation.
[b] Gal/Mcf to each stage.

TABLE VI

Effect of Limestone Type and Size on SO_2 Removal[a]

	Calcitic			Dolomitic, hard
	Hard		Chalk	
Particle size, mesh	76% -200	92% -325	96% -325	92% -325
SO_2 removal, %	78[b]		83	78

---

[a] L/G = 72. Stoichiometry: 1.0. Two-stage closed loop.
[b] Three different quarries.

Data on effect of stoichiometry are given in Figure 10. For tests at less than stoichiometric, the removal increased almost linearly with amount of limestone fed. Above 1.0 the effect was small; however, test conditions were such that excellent removal was obtained at 1.0 and there was not much room for further improvement.

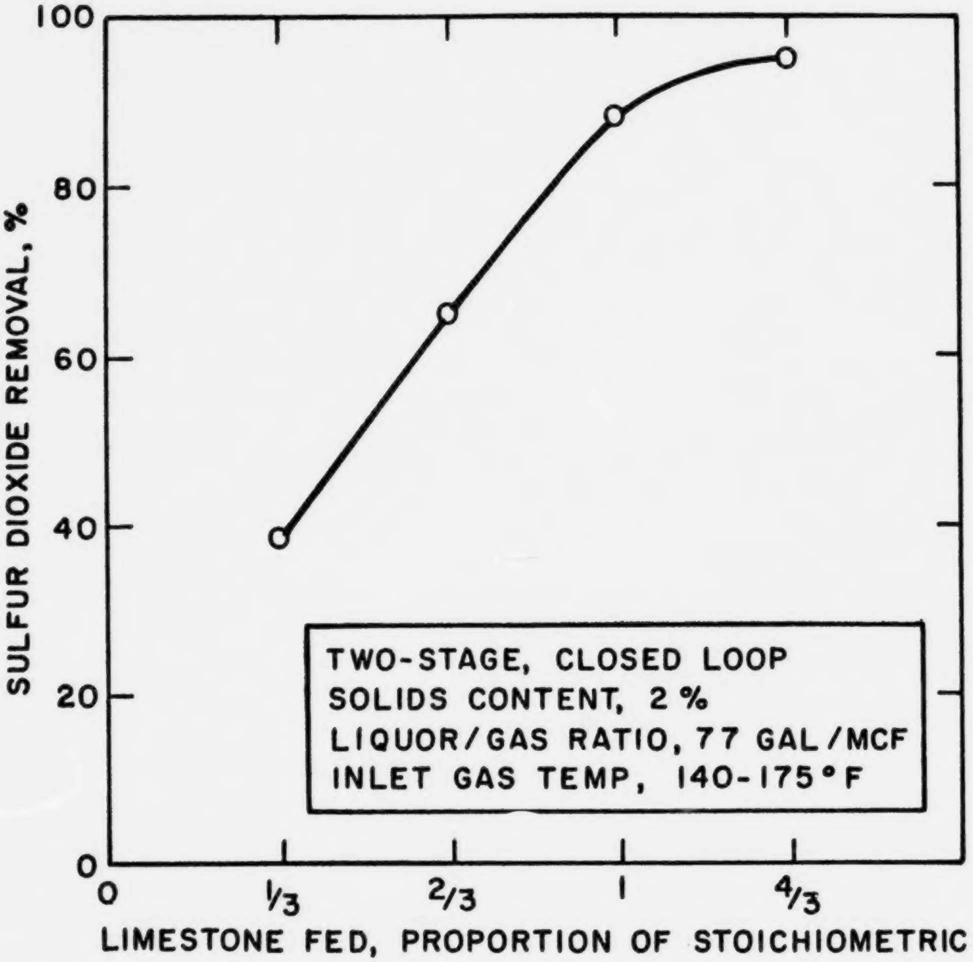

FIGURE 10

Effect of Stoichiometry on SO_2 Removal by Limestone Slurry Scrubbing

In the pilot plant work (see paper in this symposium: "Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: TVA Pilot Plant Tests--Part I, Scrubber-Type Comparison" by T. M. Kelso, P. C. Williamson, and J. J. Schultz), there has been some indication that operation with excess limestone (perhaps as high as 1.5 stoichiometric) may be advisable to ensure that conditions do not develop which cause the pH to become unstable. If this is borne out by further tests, then the effect of stoichiometry on SO_2 removal becomes a secondary consideration.

Liquid:Gas Ratio: The amount of slurry holdup in the scrubber, which is the major factor in surface area holdup, depends on scrubber type and on circulation rate. Very few data are available regarding effect of scrubber type on holdup and, in any event, scrubber type is likely to be dictated by scaling considerations rather than SO_2 removal efficiency.

Data on effect of slurry circulation rate (L/G) are given in Figure 6. The effect is major; in fact, slurry rate and inlet gas temperature have been the only variables with a major effect in the TVA small-scale work. This has also been the situation in the pilot plant tests. Again, high circulation may be essential for avoiding scaling, which makes its effect on SO_2 removal secondary.

Other Rate Factors

Limestone Type: It might be expected that the physical and chemical properties of the limestone, and their effect on rate of limestone dissolution, would be important rate factors. Such properties are important in the dry sorption method. Tests in the wet system with various limestones, however, have not indicated any major effect of limestone type--although the test work has not been extensive.

Examples of data from such tests are given in Table VI. The chalk used was a soft limestone that had seemed in preliminary tests to give better results than hard limestones. However, because of its softness the chalk tends to break down into very small particle size during the scrubbing operation, which may have contributed to its activity. When hard calcitic limestone was also ground to very small particle size, the SO_2 removal efficiency was the same.

Dolomite was somewhat less effective although not greatly so. This may be associated with the reportedly slow reaction of $MgCO_3$ minerals with weak acids.

The pilot plant work has supported these conclusions. No significant difference has been noted between the various hard limestones tested.

Blinding: Since pilot plant results had indicated the possibility of limestone blinding during periods of unstable pH, small-scale tests were made to explore ways for avoiding the problem. Blinding had never occurred in the previous small-scale work, presumably because conditions were such as to ensure steady pH (perhaps resulting from the relatively high liquor rate necessary in the small-scale equipment).

The pilot plant results indicated that if for some reason the pH in the loop decreases to a low level, the slurry becomes unresponsive--that is, further addition of limestone does not raise the pH to the normal level of 6.0-6.1. In tests with the small-scale scrubber, it was found that a similar unresponsive slurry could be developed by operating with a deficiency of limestone. In further studies with batches in a gas bubbler, a solution of $CaSO_3 \cdot 0.5H_2O$ in H_2SO_3 solution (pH, 2.6) was found to be also unresponsive; additions of limestone would not raise the pH above 3.6. An electron micrograph of solids from such an unresponsive slurry (Fig 11) shows that blinding of the limestone surface by calcium sulfite apparently had taken place.

In further tests, the unresponsive slurry was oxidized by bubbling air through it for 3 hours, which precipitated about 97% of the dissolved calcium as $CaSO_4 \cdot 2H_2O$. The slurry was then responsive; addition of limestone to the oxidized slurry (in which the pH had decreased to 1.9) brought the pH up to 6.2.

A possible explanation for the blinding is that if pH for some reason decreases during operation, presumably because the rate of limestone dissolution lags behind SO_2 absorption, the sulfite content of the solution increases rapidly because of higher sulfite solubility at low pH and the reservoir of sulfite present as sulfite crystals. Then when a limestone particle dissolves at its surface and forms a film around it of higher pH solution, the pH increase causes rapid sulfite crystallization at the surface and consequent blinding.

One difficulty with this postulation is that adding SO_2 to a saturated solution of $CaSO_3 \cdot 0.5H_2O$ can make the solution unsaturated. The effect is shown in Table VII. The $SO_3^=$ concentration decreases rapidly with pH by shifting back to HSO_3^-, with which it is in equilibrium (see Fig 2). Thus if the Ca^{++} concentration remains constant, or even if it increases somewhat, the $Ca^{++}/SO_3^=$ solubility product is not exceeded because of the very low $SO_3^=$ concentration.

Hence if limestone dissolution were inhibited and the pH were lowered by SO_2 absorption, the solution might well become unsaturated and would be less likely to precipitate $CaSO_3 \cdot 0.5H_2O$ than under normal operating conditions.

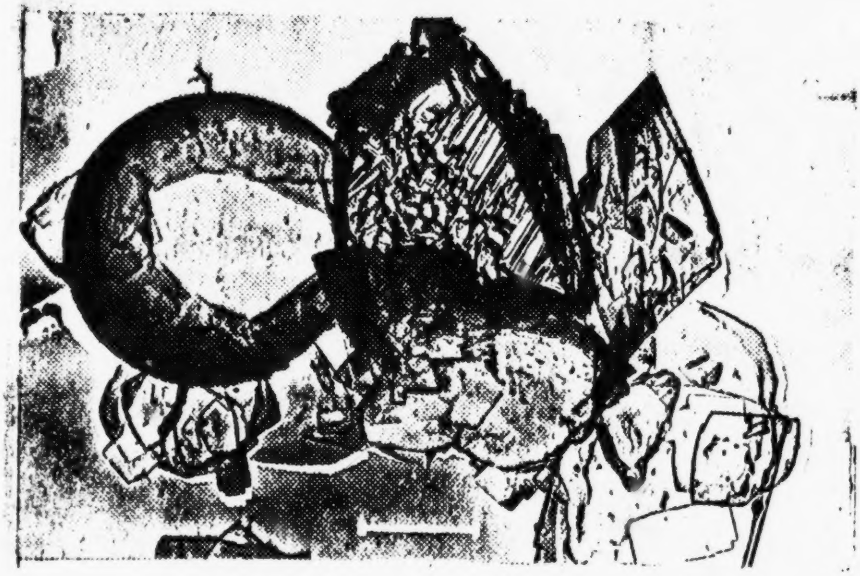

FIGURE 11

Electron Micrograph of Solids Taken from Limestone Scrubber Slurry

The particle at the right is a crystal of calcium sulfite ($CaSO_3 \cdot 0.5H_2O$). At the left is a fly ash particle and in the center is a limestone particle apparently blinded by calcium sulfite crystals growing edgewise on its surface. The scale shown is 1 micron. (Photograph from work by Dr. G. H. McClellan, TVA).

Another possibility is that the unsaturation developed at low pH may actually cause dissolution of $CaSO_3 \cdot 0.5\ H_2O$ crystals and reduce the surface area available for crystal growth. Then when $CaCO_3$ is added in the delay tank and a surface film of relatively high pH developed, the sulfite supersaturation induced by the higher pH may cause nucleation on the $CaCO_3$ surface rather than on the sulfite crystals that would ordinarily have been present. More data must be gathered before any conclusions can be made.

TABLE VII

Concentration of Sulfite Species at Constant Calcium Concentration (0.001525 m/l) but with Varying pH

	Concentration, moles/l				
pH	H_2SO_3 x 10^6	HSO_3^- x 10^{+3}	$SO_3^=$ x 10^{+5}	$CaSO_3$ x 10^5	Total SO_2 m/l x 10^3
6.0	0.27	2.24	11.80	28.37	2.649
5.0	3.49	2.94	1.57	4.33	3.005
4.0	37.2	3.14	0.17	0.47	3.188

The rapid undersaturation developed at lower pH may also explain why sulfite crystals are usually small. Even the pH variation in normal operation may cause wide swings from rapid dissolution to rapid precipitation from supersaturated solutions.

If an insufficient rate of limestone dissolution is the initial cause of the problem, then anything that increases the rate should be helpful. In the pilot plant, increase in limestone stoichiometry has been effective. Length of operating period also seems to be a factor, presumably because the ionic strength builds up and makes calcium more soluble (see later discussion).

It may be possible to ensure steady pH at lower limestone stoichiometry by feeding a little lime or ammonia along with the limestone. Tests of this procedure are planned.

There may be some blinding even at normal operating pH; adequate data for evaluating this have not yet been obtained. If so, grinding of the recycling slurry to renew the limestone surface, as practiced by Bahco /see paper by K. A. Gustavsson, "Bahco SO_2 Scrubber," presented at Internatioal Symposium on Lime/Limestone Scrubbing for SO_2 Control (sponsored by NAPCA), Pensacola, Florida, March 16-20, 1970/ may be indicated.

Ionic Strength: Increase in ionic strength by buildup in the solution of constituents such as Mg, Cl, Na, K, and NO_3 should make Ca more soluble and therefore increase the driving force for dissolution. Calculated solubilities for various ionic strengths are given in Table VIII. The data indicate an optimum level for calcium solubility.

TABLE VIII

Solubility in the System $CaO-SO_2-H_2O$ as Affected by Ionic Strength and pH

	Ionic strength					
	0.004-0.04[a]		1.0[b]		4.0[b]	
	ppm		ppm		ppm	
pH	Ca	SO_2	Ca	SO_2	Ca	SO_2
6.0	61	170	135	360	92	236
5.0	181	558	353	1093	231	711
4.0	667	2139	1077	3446	701	2334

[a] In the system $CaO-SO_2-H_2O$.

[b] Ionic strength increased by adding noncomplexing ions such as Cl^- and $N(CH_3)_4^+$.

In the small-scale work, the simulated nature of the stack gas--and the consequent absence of ionizable impurities such as carried in actual stack gas--keeps the ionic strength from building up. Tests were run, therefore, in which the ionic strength was varied by adding various amounts of magnesium sulfate (Fig 12). An optimum level of ionic strength is indicated at about 1.0.

The pilot plant tests have given the opportunity of determining the degree to which ionic strength will build up in actual operation, considering the fact that part of the solution is purged with the wet solids and replaced with water. Extended round-the-clock runs have indicated that steady state in regard to ionic strength is attained in a day or so; there is little further change in the concentration of constituents such as Mg, Fe, Na, Mn, K, and Cl. There has also been little variation in Ca and total S, although these are subject to change with minor variations in pH. Average composition over a 2-week run is given in Table IX.

The ionic strength of this solution is about 0.120, considerably below the indicated optimum. The only apparent way to increase it is to bleed less liquid phase with the solids, but the 60% liquor content of the purged solids obtained in the current tests may be difficult to reduce.

Inlet SO_2 Concentration: In the usual gas scrubbing situation, a decrease in inlet concentration of the constituent to be absorbed would be expected to decrease the percentage absorption because of the lower driving force for gas-liquid transfer. For limestone slurry scrubbing of SO_2, however, the role of solid-liquid transfer complicates the situation.

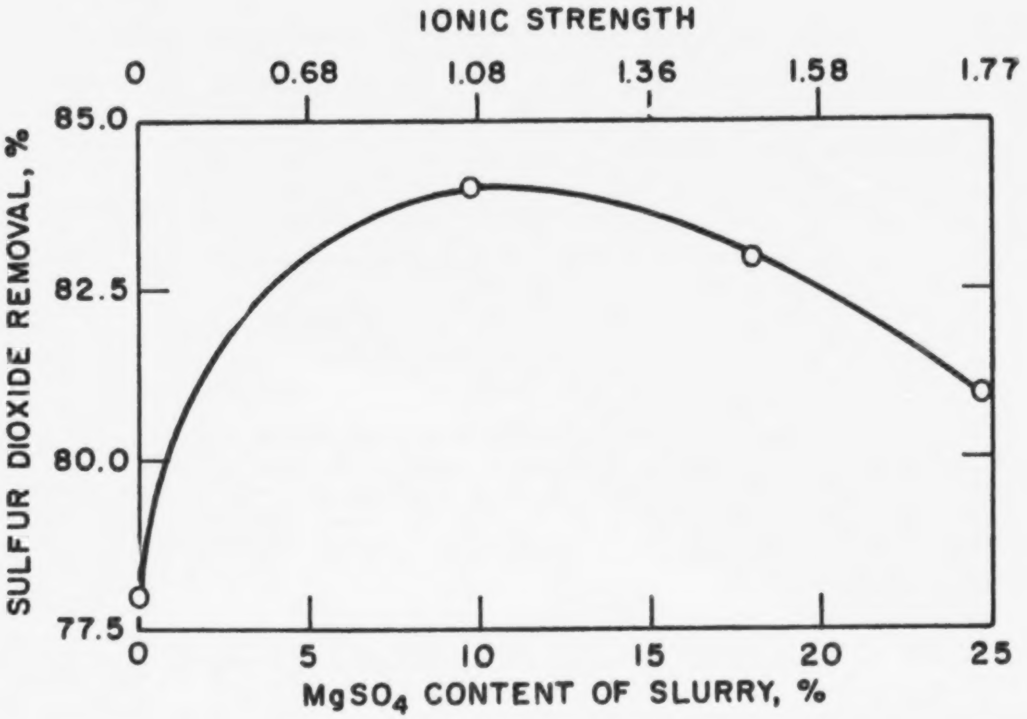

FIGURE 12

Effect of $MgSO_4$ Addition on SO_2 Removal

in Closed-Loop Limestone Slurry Scrubbing

TABLE IX

Average Filtrate Composition Over 2-Week Pilot Plant Run[a]

Constituent	Concentration, gpl
Ca	1.06
Mg	0.46
Total S	0.91
Fe	0.001
Na	0.038
Mn	0.002
K	0.059
Cl	1.32
Total N	0.04

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[a] Limestone stoichiometry: 1.5. L/G: About 40 gal/Mcf. Solids content of slurry: 12-15%. Water content of purged solids: About 60%. Samples taken at scrubber outlet.

Data from tests on effect of inlet SO_2 concentration are given in Figure 13. The percentage removal was actually higher for the lower concentrations, probably because of the smaller amount of limestone dissolution required per unit volume of slurry (the liquor rate was the same for all of the tests). The effective surge tank volume (gal/lb SO_2·min), which has been shown to be important, was much higher at the lower SO_2 concentrations (range from 1240 to 4900 gal/lb SO_2·min).

Thus it appears that low exit SO_2 concentrations, on the order of 50 ppm or less, can be attained with high liquor rate and surge tank retention time.

Waste Disposal

As noted earlier (Fig 11), the calcium sulfite crystals formed in limestone scrubbing are very small, thin platelets. When the slurry is allowed to stand, the crystals settle rapidly for a short time--giving a fairly clear supernatant layer--but the settling rate then drops off sharply. It is postulated that the decreased rate begins when the crystals start touching each other; a voluminous, gel-like structure develops in which settling is relatively slow.

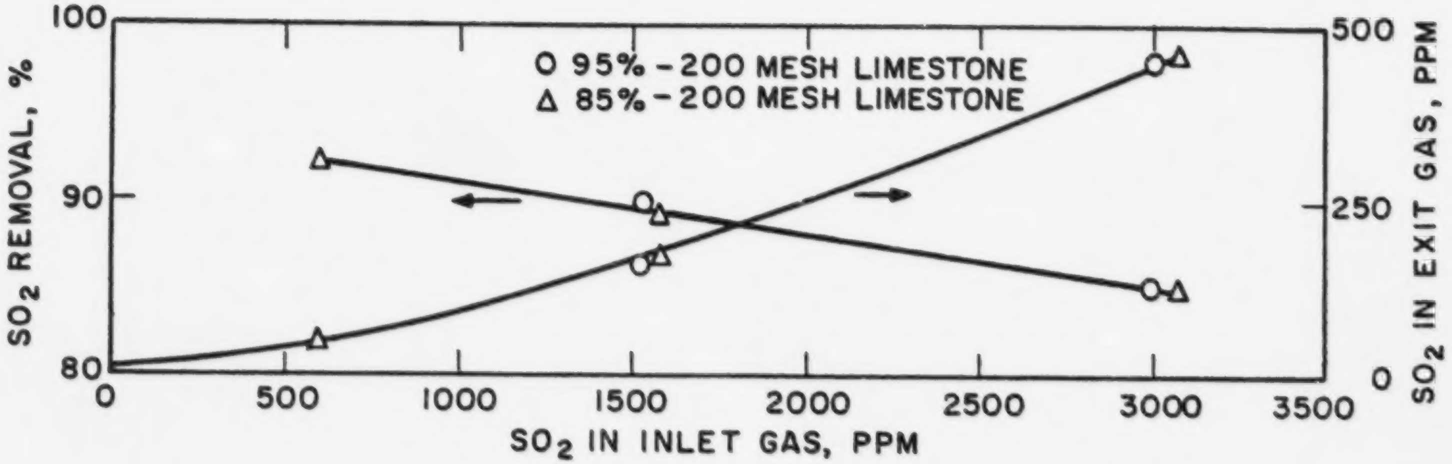

FIGURE 13

Effect of Inlet SO_2 Concentration on SO_2 Removal with Two-Stage Closed-Loop Limestone Slurry Scrubbing

The liquor:gas ratio was 80 gal/Mcf, the solids content of the slurry 2%, and the inlet gas temperature 150-200°F.

In small-scale tests with the slurry, it was found that the average rate of free settling was about 2 in./hr; this rate was fairly uniform as long as the free settling phase lasted. A sample of the gel formed (16% solids) after compressive settling began was tested with a gelometer; gel strength increased with time, as follows.

Time elapsed after stirring, min	Yield point, g-cm
0	0
30	6
60	9
1080	25

Settling of the gel could be accelerated by periodic slow stirring to destroy the gel structure. A gel that had settled to 38% solids and showed no indication of further significant settling was settled to 48% solids by three stirrings about a day apart.

Oxidation was quite effective in promoting settling. Further work will be done on this approach.

Alkali - Lime-Limestone

The many problems involved in lime-limestone scrubbing make it quite desirable to find a better throwaway method. Several organizations, including TVA, are working on a process that involves scrubbing with an alkali solution (NH_4, Na, K) and regenerating the alkali with lime or limestone. The waste product is calcium sulfite (plus calcium sulfate, hopefully) as in straight lime-limestone scrubbing. Keeping the lime-limestone out of the scrubber should greatly reduce the problems of scaling, erosion, silting, wet-dry deposition of solids, particulate entrainment, and high pumping cost.

Of the various alkalies, Na and K have the advantage that they are not volatile as is NH_3 -which simplifies scrubber design and operation. However, sulfate formed by oxidation in the scrubber is quite difficult to regenerate; there have been efforts over the last several decades to convert byproduct sodium sulfate to caustic soda without success. Regeneration in an SO_2 scrubbing loop may be feasible, however, because only a partial conversion per pass is acceptable, but it is likely that the resulting NaOH solution would be quite dilute and that circulation rate might therefore have to be high.

If ammonia is used as the alkali, regeneration may be somewhat easier since $(NH_4)_2SO_4$ can be crystallized from a sidestream and sold (whereas Na_2SO_4 would have a quite limited market). Or the $(NH_4)_2SO_4$ can be reacted with lime to regenerate the ammonia, as in the Kuhlmann Electricite de France process.

In the TVA small-scale work, limestone rather than lime has been used as the regenerant since it is cheaper. It reacts well with alkali bisulfite (Fig 14) but not with sulfite; however, the sulfite can be recirculated to the scrubber as is the common practice in alkali scrubbing processes of the recovery type.

The data in Figure 14 indicate that the regeneration temperature should be somewhat elevated; fortunately, in power plant stack gas scrubbing heat from the stack gas gives an adequate liquor temperature level, which may not be true for other types of stack gas.

Since the calcium sulfite formed in the tests settled well, no difficulty is expected in separating and washing the waste solids. Further work will be concerned with separation of $(NH_4)_2SO_4$. Data on the ammonia scrubbing step is being obtained in the current EPA-TVA ammonia scrubbing pilot plant project. Testing of the integrated process is planned in a TVA pilot plant now under construction.

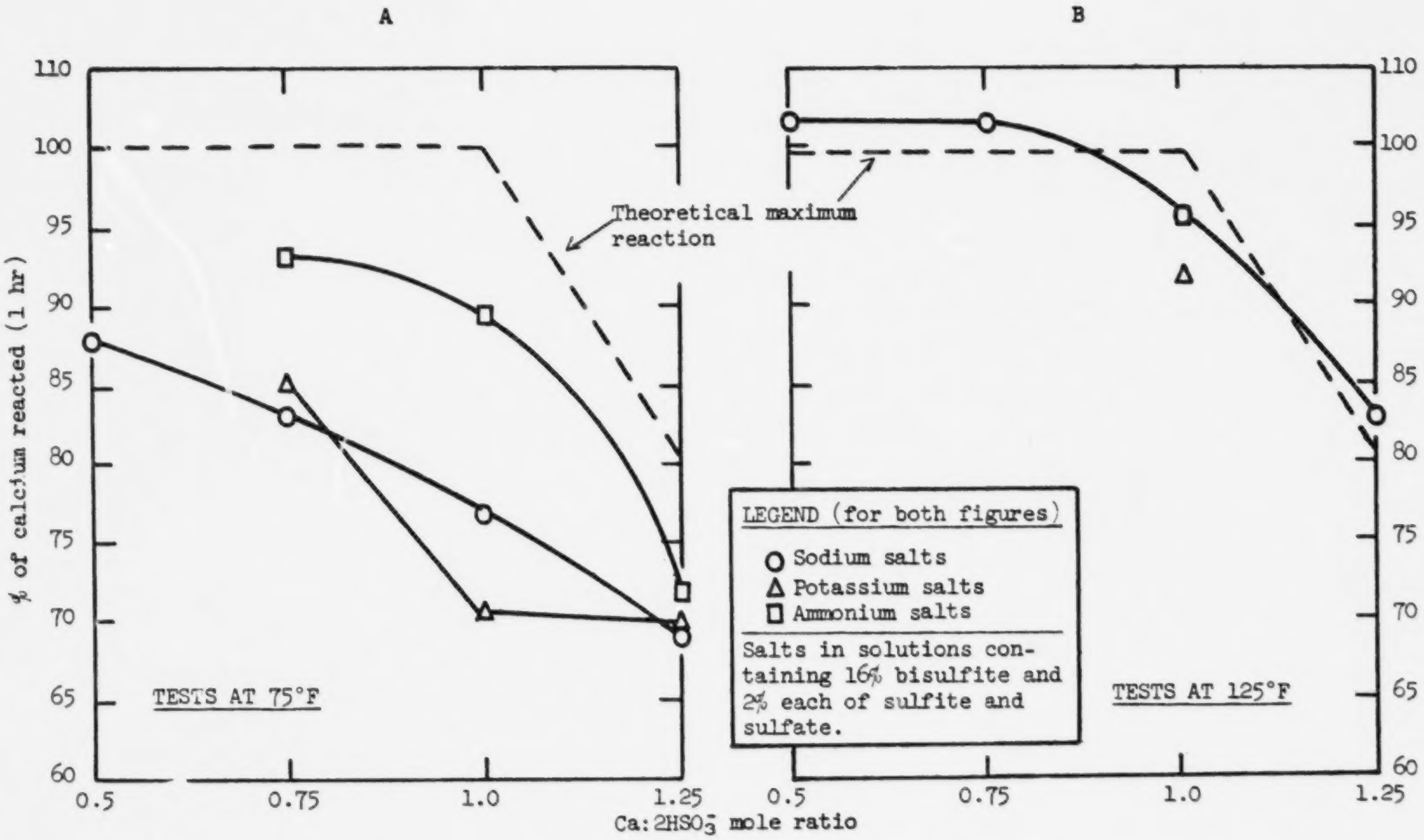

FIGURE 14

Effect of Calcium Carbonate Proportion on Degree of Reaction with Solutions of Alkali Bisulfite-Sulfite-Sulfate Salt Mixtures

Absorption Studies of Equimolar Concentrations of NO and NO_2 In Alkaline Solutions

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ABSTRACT

ABSORPTION STUDIES OF EQUIMOLAR CONCENTRATIONS OF NO & NO_2 IN ALKALINE SOLUTIONS

Equimolar concentrations of NO and NO_2 in flue gas were passed countercurrently to various alkaline solutions in a bench-scale packed column. The concentrations of NO and NO_2 studies were from 250 ppm to 750 ppm each. Liquid velocity, gas velocity, size of packing, and liquid temperature were the parameters varied.

The results of this experimentation indicates that at a concentration of 250 ppm each of NO and NO_2 in flue gas the percent removal for NO and NO_2, expressed as total NO_x was between 12 to 14 percent; at 500 ppm each of NO and NO_2 in flue gas, the percent removal was between 17 to 19 percent; at 750 ppm each of NO and NO_2 in flue gas, the percent removal was between 27 to 29 percent.

Absorption Studies of Low Concentrations of NO and NO_2 in Alkaline Solutions

BACKGROUND

The Federal Government has enacted legislation to regulate and control the levels of nitrogen oxides in the ambient air and to limit their emission from specific new stationary sources. The control of nitrogen oxides is important because these air pollutants are involved in the complex photochemical reactions in the atmosphere which result in smog formation and because, by themselves, they have adverse physiological effects for all forms of life. Although a number of oxides of nitrogen are recognized, the most common forms are nitric oxide (NO) and nitrogen dioxide (NO_2) on account of their widespread production and their relatively high atmospheric stability. In this paper the term "nitrogen oxides (or NO_x)" refers to either or a combination of these two gaseous air pollutants.

Mobile sources, the largest single source category, contribute over 40 percent of all the man-made NO_x emitted in the United States. Current knowledge on the methods of control are covered in detail in AP-66, "Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources." The next largest source is electric power generation, which is responsible for nearly 20 percent of all man-made NO_x. About 40 percent of NO_x emitted from stationary installations is attributed to electric generating power plants. Control of NO_x from stationary sources is discussed in detail in AP-67, "Control Techniques for Nitrogen Oxide Emissions from Stationary Sources."

About 1 percent of the total man-made NO_x emitted to the ambient air of the United States is formed by chemical sources, mainly related to the manufacture and use of nitric acid. Concentration from these sources are usually much greater, however, than those from combustion sources, and as a consequence, these sources often give rise to a highly visible, brown-red gas.

THEORETICAL CONSIDERATIONS

Under proper conditions, nitrogen and oxygen tend to combine in accordance with the following equation:

$$N_2 + O_2 \rightarrow 2NO$$

The equilibrium concentration of NO varies with temperature; it is negligible below 1,000°F but quite significant above 3000°F. In addition, it is influenced by gas composition; at a given temperature, for example, the equilibrium concentration of NO in air exceeds that of NO in flue gas of 3 percent oxygen content by a factor of approximately 3.

Nitric oxide tends to react with oxygen as follows:

$$2NO + O_2 \rightleftharpoons 2NO_2$$

This equation implies the coexistence of NO and NO_2. Calculated equilibria indicate that the stability of NO_2 decreases with increasing temperature. Nevertheless, from an equilibrium standpoint, the absolute concentration of NO_2 increases with temperature while the ratio of its concentration to that of NO decreases with increasing temperature.

Chemical equilibria depend on the initial and final conditions and not at all on reaction mechanisms or intermediate reaction steps. Equilibrium concentrations are obtained after the lapse of sufficient reaction time; therefore, they are not necessarily observed experimentally. Because of the simplicity of the molecules involved in the previous equations, their thermodynamic properties are accurately known and equilibrium calculations are made easily.

It has been suggested(1) that equimolar mixtures of NO and NO_2 might be removed by scrubbing with alkaline solutions. The use of the alkaline materials (NaOH and Na_2CO_3) for NO_x scrubbing was studied originally by Sherwood and Pigford (2) who found, using a concentration of one percent NO_x in the gas phase, that a 46 percent NaOH solution absorbed nitrogen oxides from a gas containing equimolar quantities of NO and NO_2 at rates as much as ten times faster than if NO_2 were present alone. When they compared the NO + NO_2 absorption rates with the calculated equilibrium concentration of N_2O_3 ($NO + NO_2 \rightarrow N_2O_3$), it was found that the rate was approximately proportional to the first power of the N_2O_3 concentration, indicating that this was the reacting species. Ganz and co-workers(3-6) performed similar studies using sodium carbonate solutions and reached similar conclusions. Andrew and Hanson(7) describe the dynamics of nitrous gas absorption into water as the result of a number of separate reaction mechanisms, and state that relative importance of these mechanisms is primarily dependent on the gas composition.

In order to determine the applicability of aqueous alkaline scrubbing of equimolar NO/NO_2 mixtures at typical flue gas concentrations, the EPA laboratories decided to study the absorption of NO and NO_2 at concentrations in the range of 250 ppm to 750 ppm each in flue gas.

Although control of most of the NO_x emissions from combustion sources is expected to be achieved by various combustion modification or control methods, additional flue gas or process stream treatment methods may be required for specific problem areas. Consequently, a limited effort has been directed to research leading to the identification and development of effective flue gas treatment techniques for NO_x control.

Rates of formation can be calculated by kinetic equations that rely heavily on experimental measurements. The reaction products depend to a large measure on the relative speeds of the reactions that actually occur. The rate of oxidation of nitrogen to NO is highly temperature-dependent; it is very slow at 500°F, but fast at 4000°F. The underlying reason is that a high level of energy is needed to break the N-N (dissociation energy 225.3 kcal/mole) triple bond of molecular nitrogen so that oxygen can react. Conversely, a smaller but still relatively large amount of energy is needed to break the N-O bond to permit decomposition of nitric oxide into its elements. This means that high temperatures are required to form NO; once formed, it resists any breakdown into its elements. Breakdown becomes more and more unlikely as temperature decreases, because the energy available for thermal breakdown diminishes rapidly with decreasing temperature. Thus, an initially high temperature followed by quick cooling, even to a relatively high temperature level, produces large amounts of NO.

At temperatures above 2000°F, both NO and NO_2 are formed, but the amount of NO_2 is usually less than 0.5 percent of the total NO_x. The oxidation of NO to NO_2 by oxygen, however, is peculiar in that the rate of reaction decreases with increasing temperature. This is one of the few known reactions that exhibit an inverse temperature relationship. The resultant slow oxidation rate at high temperatures accounts in part for the negligible amounts of NO_2 frequently found in hot combustion gases. Another characteristic of the oxidation of NO to NO_2 is the fact that the rate varies with the square of the NO concentration. The rate of oxidation of NO by oxygen in air falls off rapidly, therefore, with dilution of the NO. A long period of time may be required to oxidize trace quantities of NO by this mechanism.

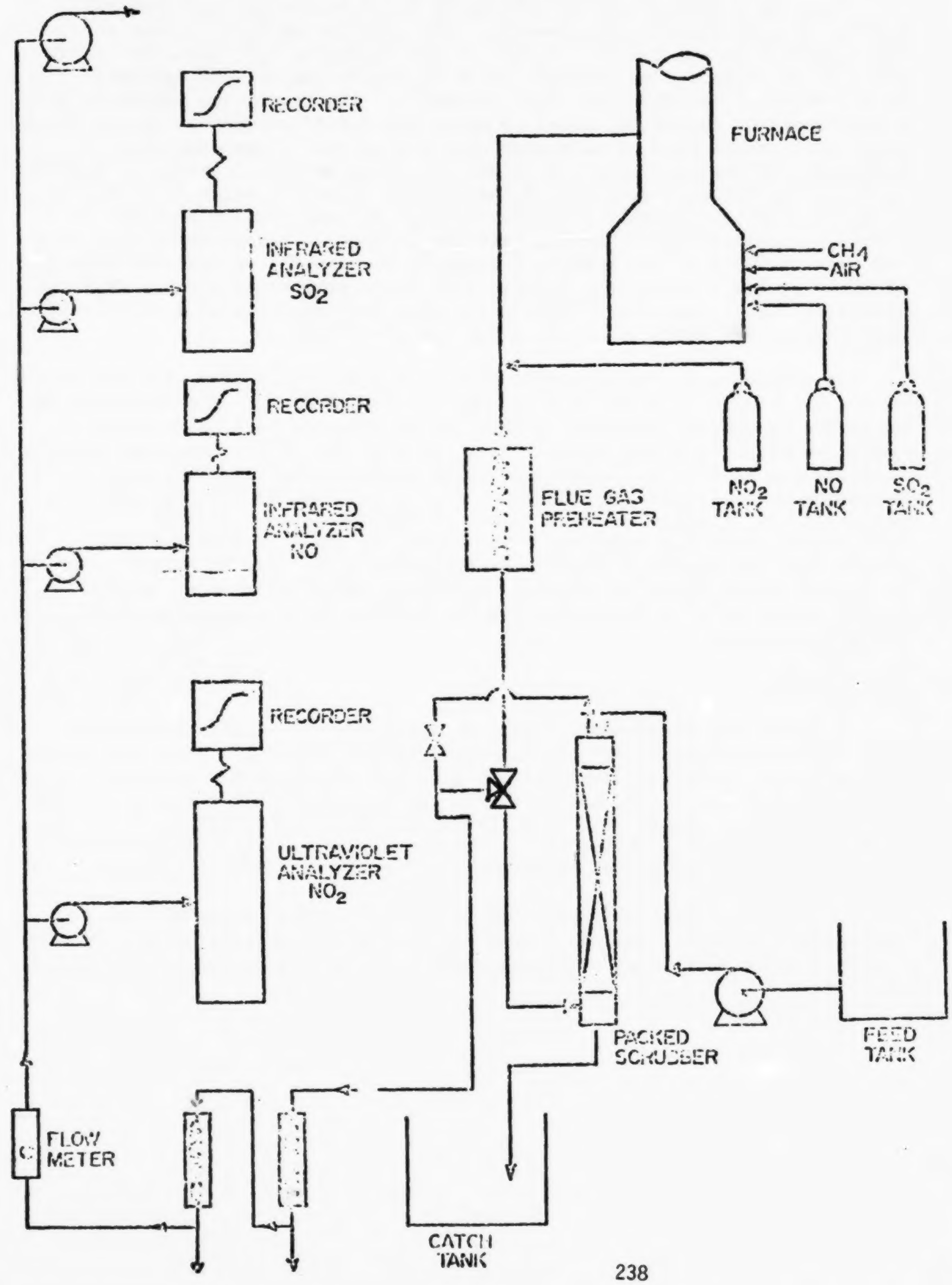
EXPERIMENTAL

A laboratory bench-scale packed scrubber was fabricated (see Figure 1). The scrubber consisted of a glass (Pyrex) column 2 1/4 inch I.D. packed with eighteen inches of 3/8-inch Berl saddles. The scrubber was equipped with an inlet liquid port and an outlet gas port at both the top and bottom of the scrubber. Because of this, the laboratory bench-scale scrubber was capable of passing scrubbing liquor cocurrently as well as countercurrently to the gas flow over a wide range of liquid to gas (L-to-G) flow rates.

In the bench-scale packed scrubber, the following parameters can be varied and measured: gas and liquid flow rates, concentrations of the gaseous pollutants, packing height, type of packing, temperature, and concentration of alkali.

FIGURE I

FLOW DIAGRAM OF EQUIPMENT USED FOR ABSORPTION OF NO & NO_2



The main objective of these studies was to determine the rate of mass transfer for equimolar concentrations of NO and NO_2 in the range of 250 ppm to 750 ppm each. The parameters affecting the rate of mass transfer were determined by a study of the following: gas and liquid velocitiies, types (i.e., $Ca(OH)_2$, $Mg(OH)_2$, and NaOH) and concentrations of scrubbing solutions, temperature, and mole ratios of NO and NO_2, size of packing, and height of packing.

TESTING

These studies were performed using flue gas from the combustion of natural gas (see Figure 1). Air, natural gas, and NO were blended and burned, (NO_2 was added prior to entry to the preheater to minimize thermal decomposition of NO_2 to NO), to give a standard flue gas having the following approximate composition: CO_2, 6.4%; O_2, 3.0%; H_2O, 12.7%; N_2, 74.9%; NO, 0.025 to 0.075%; and NO_2, 0.025 to 0.075%. The two gas flow rates used were 20 SCFH and 30 SCFH. The two liquid flow rates were 170 ml/min and 350 ml/min. These combinations of gas and liquid flow rates correspond to a range of L-to-G ratios from 9.3 to 29.2. A flue gas preheater was used to raise the temperature of the gas entering the scrubber to 350°F. After passing the gas countercurrently to the liquid flow through the scrubber, the gas was pulled through two condensers to remove water since water interferes with the monitoring of NO and NO_2. Several monitors were used to follow the concentration changes of the gaseous components of primary interest. A non-dispersive infrared spectrophotometer, that provided continuous SO_2 measurement, was installed in case of SO_2 fluctuations in the natural gas supply. During the course of these measurements, no appreciable content of SO_2 was observed in the flue gas. Another infrared instrument provided continuous NO measurement, and an ultraviolet spectrophotometer provided continuous NO_2 measurement. The specific instruments used in these tests were Beckman Model 315A Infrared Analyzers for SO_2 and NO and a DuPont Model 400 Ultraviolet Analyzer for the NO_2 measurement. By proper selection of flow paths using a three-way valve (see Figure 1), the gas could be monitored by the instruments prior to entry to the scrubber or after passing through the scrubber and condensers. One feed tank and one catch tank were used in these experiments. Scrubbing liquor, i.e., ($Ca(OH)_2$, $Mg(OH)_2$, or NaOH solutions, were fed on a once-through basis from the feed tank through the scrubber and into the catch tank. The temperature of the solutions in the feed tank was maintained by means of a 1000-watt electric heater which was thermostatically controlled to ±5°F. The range of temperatures over which this heater operated was from 100°F to 200°F.

A run was performed in the following manner. The feed tank was charged with fifteen gallons of distilled water and heated to 100°F, 125°F, or 150°F, while stirring. After the water reached the desired temperature, the solid alkaline material was added to the feed tank. The amount of $Ca(OH)_2$ or $Mg(OH)_2$

added was equal to that amount necessary to make fifteen gallons of solution saturated with the alkaline material at the particular operating temperature. The concentrations of NaOH solutions were from 10^{-4} N solutions to 5% solutions. After the pH of the solution reached a maximum value, i.e., about fifteen minutes, the alkaline solution (of either $Ca(OH)_2$, $Mg(OH)_2$, or NaOH) was then pumped into the top of the scrubber at either 170 ml/min or 350 ml/min/ As soon as the temperature in the packed bed of the scrubber reached within ± 2°F of the liquid temperature of the feed tank, the three-way gas feed valve was switched and the NO- and NO_2- containing flue gas was fed to the bottom of the scrubber. The gas leaving the top of the scrubber was monitored for NO, NO_2 and SO_2 as mentioned previously. The time for the SO_2 and NO to go from the furnace to the monitoring instruments was twelve seconds at 20 SCFH, and six seconds at 30 SCFH. The time for the NO_2 to go from the preheater to the instruments was approximately ten seconds at 20 SCFH, and five seconds at 30 SCFH.

ANALYTICAL PROBLEMS OF SCRUBBING STUDY

A. Gas Analysis

The results of engineering studies can be no better than the analytical tools used to obtain these results. In the study of NO_x scrubbing with a packed bed reactor, a proper interpretation of NO and NO_2 concentrations (as obtained from the non-dispersive infra red analyzer and the ultraviolet spectrophotometer, respectively) is dependent upon the specificity of the instrument for the species being studied. NO_x chemistry is very complex and a large number of equilibria occur simultaneously, i.e.,

$$2\,NO_2 \rightleftharpoons N_2O_4$$

$$NO + NO_2 \rightleftharpoons N_2O_3$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$3NO_2 + H_2O \rightleftharpoons 2NO_3^- + 2H^+ + NO$$

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$$

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + 2NO + H_2O$$

and others.

During the course of packed bed scrubbing studies, scrubbing efficiency is determined by comparing the data for the scrubbed gases with those obtained from by-passing the scrubber and passing the NO_x containing flue gas into the analyzers directly. It was found that the total NO_x determined by the analyzers was greater than the sum of the entering NO and NO_2 concentrations. It was subsequently deduced that the NDIR was sensing N_2O_4 as well as the NO which it was designed to determine. This interference was eliminated by raising the temperature of the gas going to the NDIR, thus, decomposing any N_2O_4

to NO_2. It was believed advisable also to raise the temperature of the gas sample seen by the UV NO_2 analyzer. This was done to avoid any possibility of interference by N_2O_3 or N_2O_5 with the determination of NO_2.

It was decided that, because of possible interference problems with the process monitors, a basic standard method was needed to establish the accuracy of the monitors when used under various experimental conditions. The first approach to a solution of this problem involved gas chromatography. A method was developed in which the gas sample was separated on a Porapak Q column (1 ft x 1/8 in.) at 30°C. With this procedure it is possible to determine NO in NO-N_2 mixtures if the NO concentration exceeds 8000 ppm. This lack of sensitivity causes the gas chromatographic approach to be inappropriate for levels of NO normally found in flue gas.

The second approach at a standard method to check out the accuracy of the NO_x monitors involved the use of chemiluminesence. An instrument built by the Division of Chemistry and Physics was borrowed and comparisons made to the process monitors. After the modifications of the process monitors previously mentioned were completed, the concentrations determined by the monitors were identical to results determined by chemilumenesence. This calibration yielded satisfactory results for the process monitors in that material balances in the gas phase could then be achieved.

B. Liquid Analysis

A liquid analysis for NO_2 and NO_3 described by Walters and Uglum[8] was performed on the scrubber solution when water or NaOH solutions were used. This liquid analysis did not yield acceptable results with $Ca(OH)_2$ and $Mg(OH)_2$ solutions. The chief problems which were encountered were caused by precipitation from the saturated solutions being used for scrubbing in the cuvette causing erroneous results. No liquid analyses were reported in this paper due to the variation in instrument readings caused by this precipitation.

DISCUSSION AND RESULTS

Figures 2 through 18 are plots of all the data. The ordinate of these figures is the rate of absorption of NO and NO_2 per hour per scrubber cross-sectional area. The abscissa is the mole percent of NO and NO_2 in the flue gas stream.

Many of the figures indicate a slurry flow or liquid rate of 170 and 350 ml/min. Two figures could have been drawn showing that the data points would have been identical to each other at the two slurry or liquid flow rates. It was found during this work that slurry flow rate had no effect on the adsorption rate of NO_x. Consequently, many of the figures indicate flow rates of both 170 and 350 ml/min where the other parameters and resultant adsorptions are replicated. Instead of making two different figures, it was decided to make one figure.

Figures 2 through 8 show the rate of absorption of NO and NO_2 in flue gas with use of saturated solutions of magnesium hydroxide under various conditions. The parameter changed in Figures 2 and 3 was the gas flow rate i.e., from 20 SCFH to 30 SCFH. As can be seen from these figures, there is no apparent change in the rate of absorption of NO and NO_2 with gas flow rate. Also, it should be pointed out that changing the slurry or liquid flow rate from 170 ml/min to 350 ml/min produced no change in absorption. In Figures 4 and 5 the parameters changed were liquid or slurry temperature and gas flow rate. The data on Figures 4 and 5 indicate no apparent change in absorption rate due to variation in slurry or liquid temperature and gas flow rate. Figures 6 through 8 shown one gross change relative to Figures 1 through 5, and that is a change in the size of packing. Four millimeter Berl saddles were used instead of the 3/8-inch Berl saddles. This change was made to see if a change in interfacial area would affect the rate of absorption.

Another change made within the data in Figures 6 through 8 was the slurry or liquid temperature. No statistical difference could be found due to a temperature effect. Comparing Figure 6 through 8 to Figures 2 through 5 where the gross change was the packing size, no statistical difference was found between the slopes of the best fit lines. Intuitively, one might conclude that increasing the interfacial area would yield an increase in the rate of absorption but there is no statistical evidence for this.

Figures 9 through 12 shown the rate of absorption of NO and NO_2 from flue gas using saturated solution of calcium hydroxide under various conditions.

The main parameter changed in Figures 9 and 10 was the gas flow rate, i.e., from 20 SCFH to 30 SCFH. No change in the absorption of NO and NO_2 was noted. Similar to the results with the magnesium hydroxide solutions, no change in absorption was noted due to the change in slurry or liquid flow rates, i.e., from 170 ml/min to 350 ml/min.

Again one main parameter was changed between Figures 11 and 12 and that was the gas flow rate i.e., 20 SCFH to 30 SCFH. No significant change in absorption was noted.

Comparing Figures 9 and 10 to Figures 11 and 12, where the main parameter changed was temperature (i.e., 125^oF to 150^oF), no statistical change was noted in the rate of absorption.

Figure 13 shows the results of the use of calcium hydroxide as a scrubbing agent while the column was packed with four-millimeter Berl saddles. It was not long before the column plugged and started to flood, yielding limited data. The plugging was caused by the reaction of calcium hydroxide with the carbon dioxide in the flue gas.

FIGURE 2

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO$_2$ AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

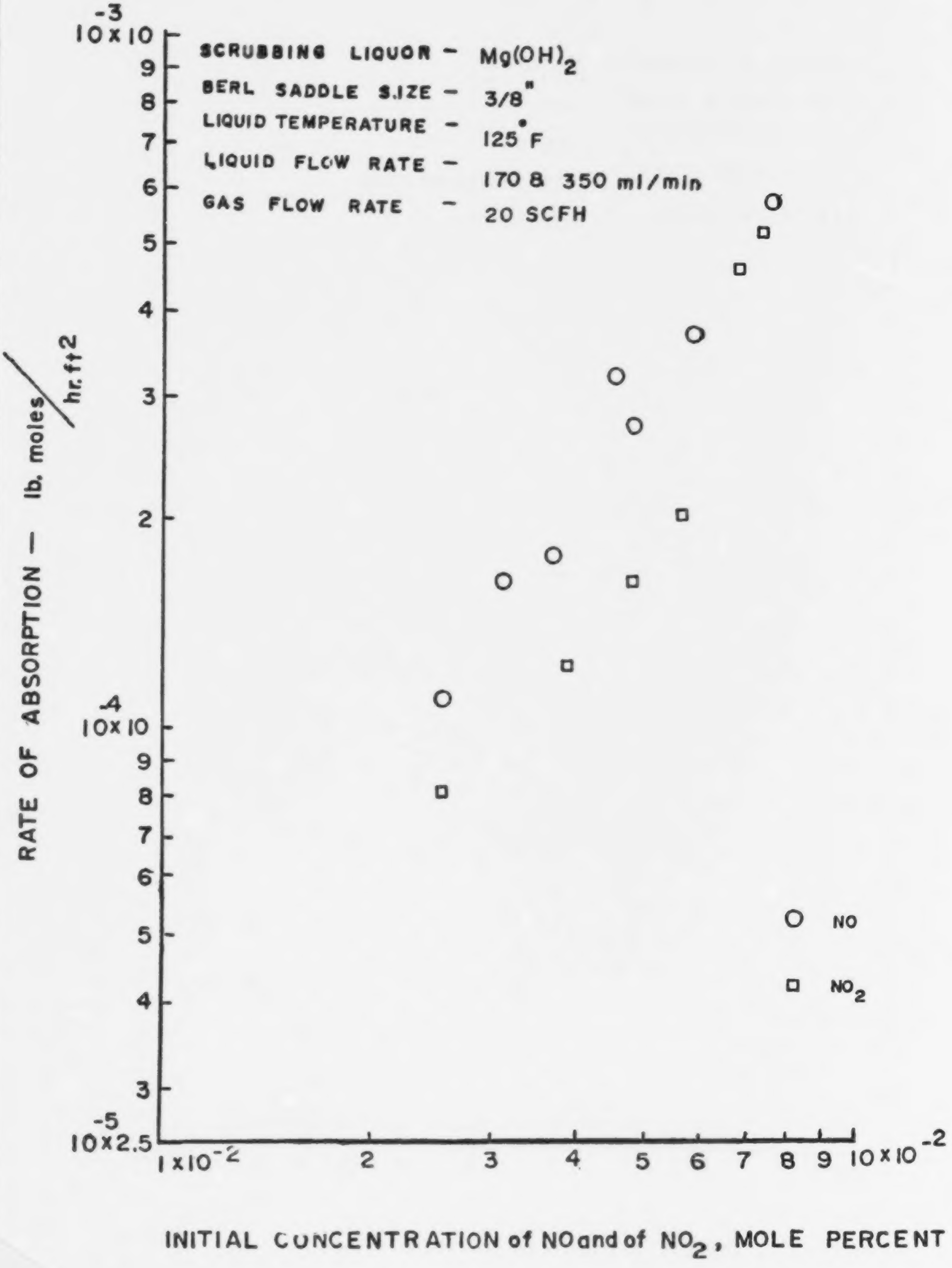
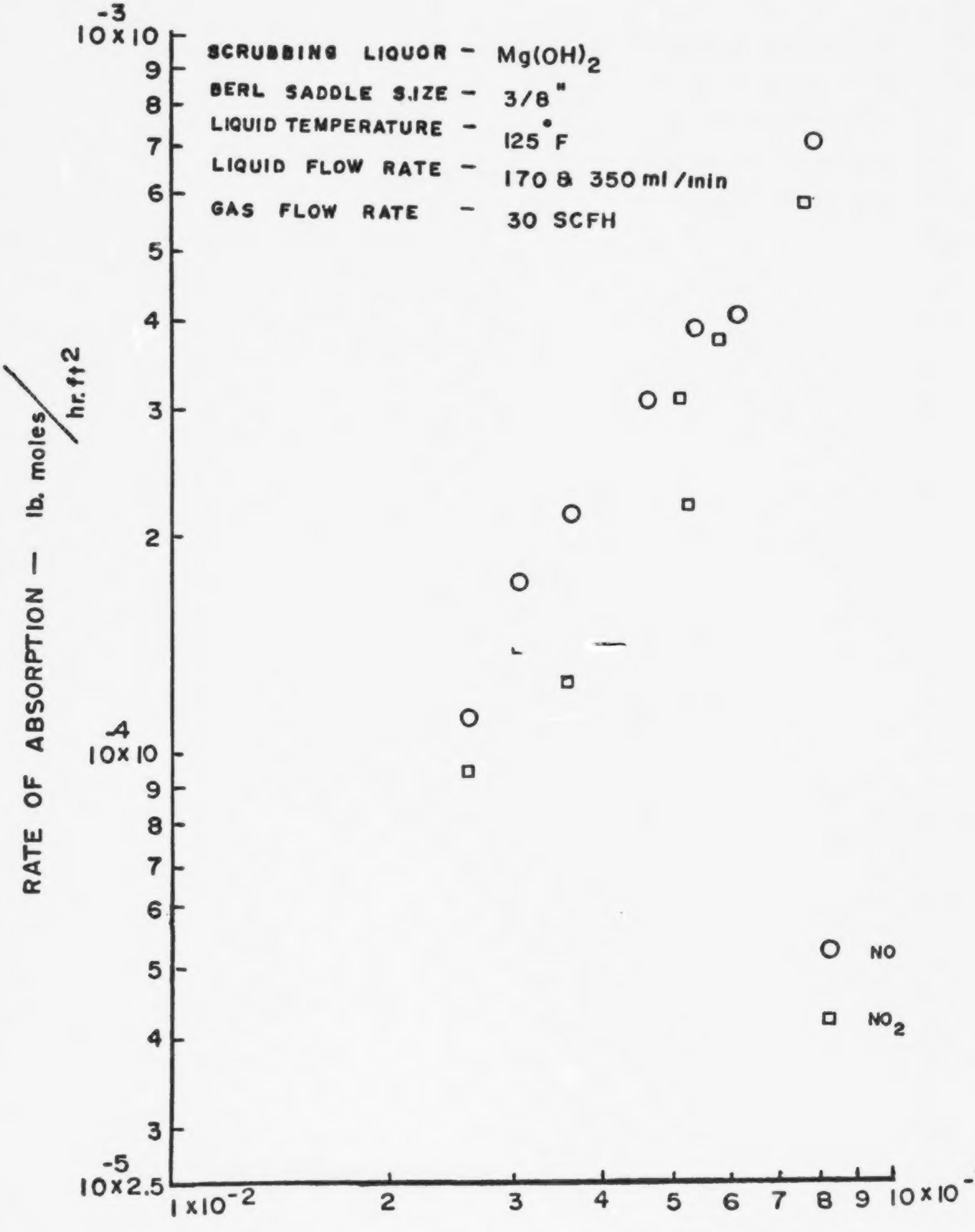


FIGURE 3

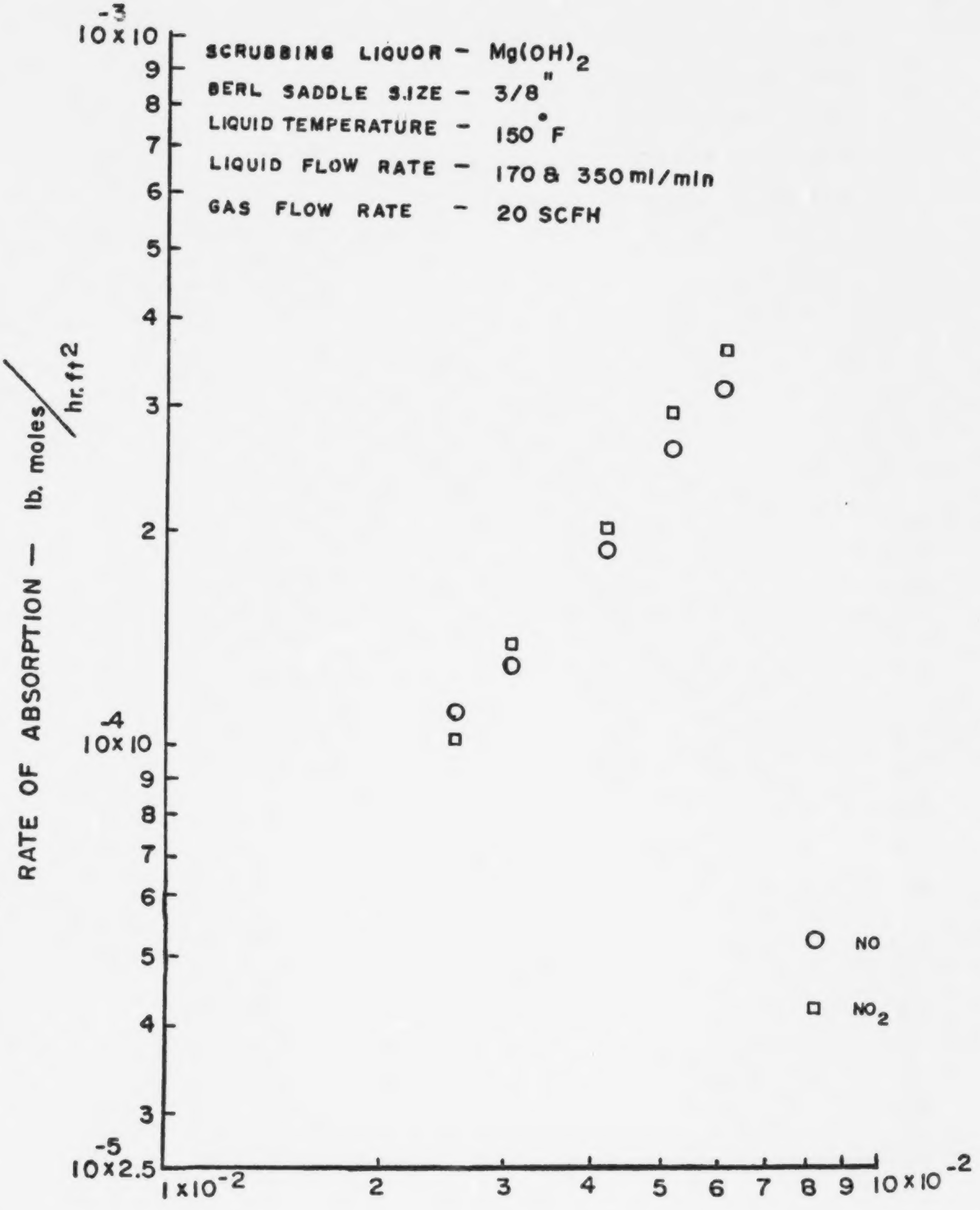
RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS



INITIAL CONCENTRATION of NO and of NO_2, MOLE PERCENT

FIGURE 4

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS



INITIAL CONCENTRATION of NO and of NO_2, MOLE PERCENT

FIGURE 5

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

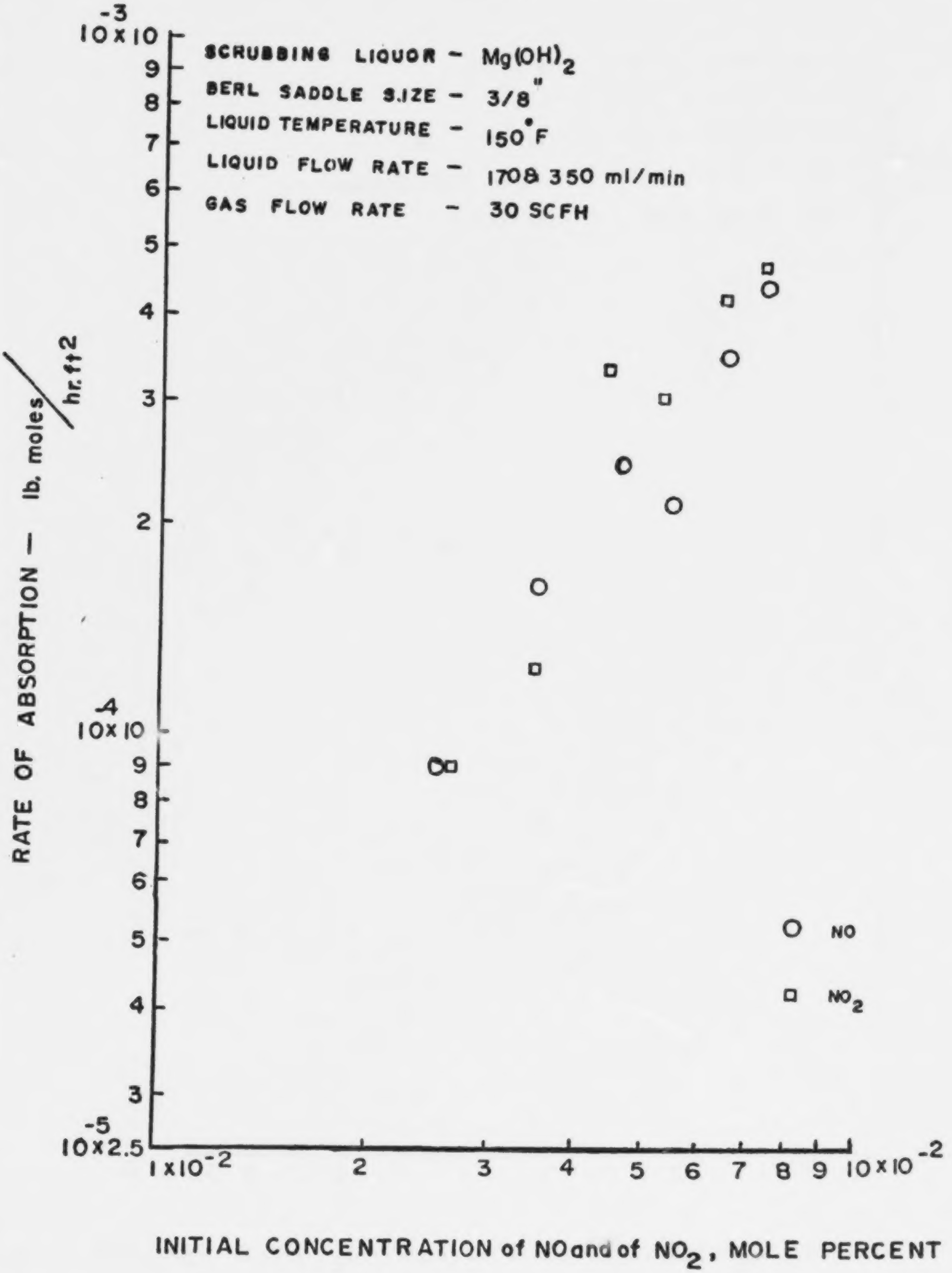


FIGURE 6

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

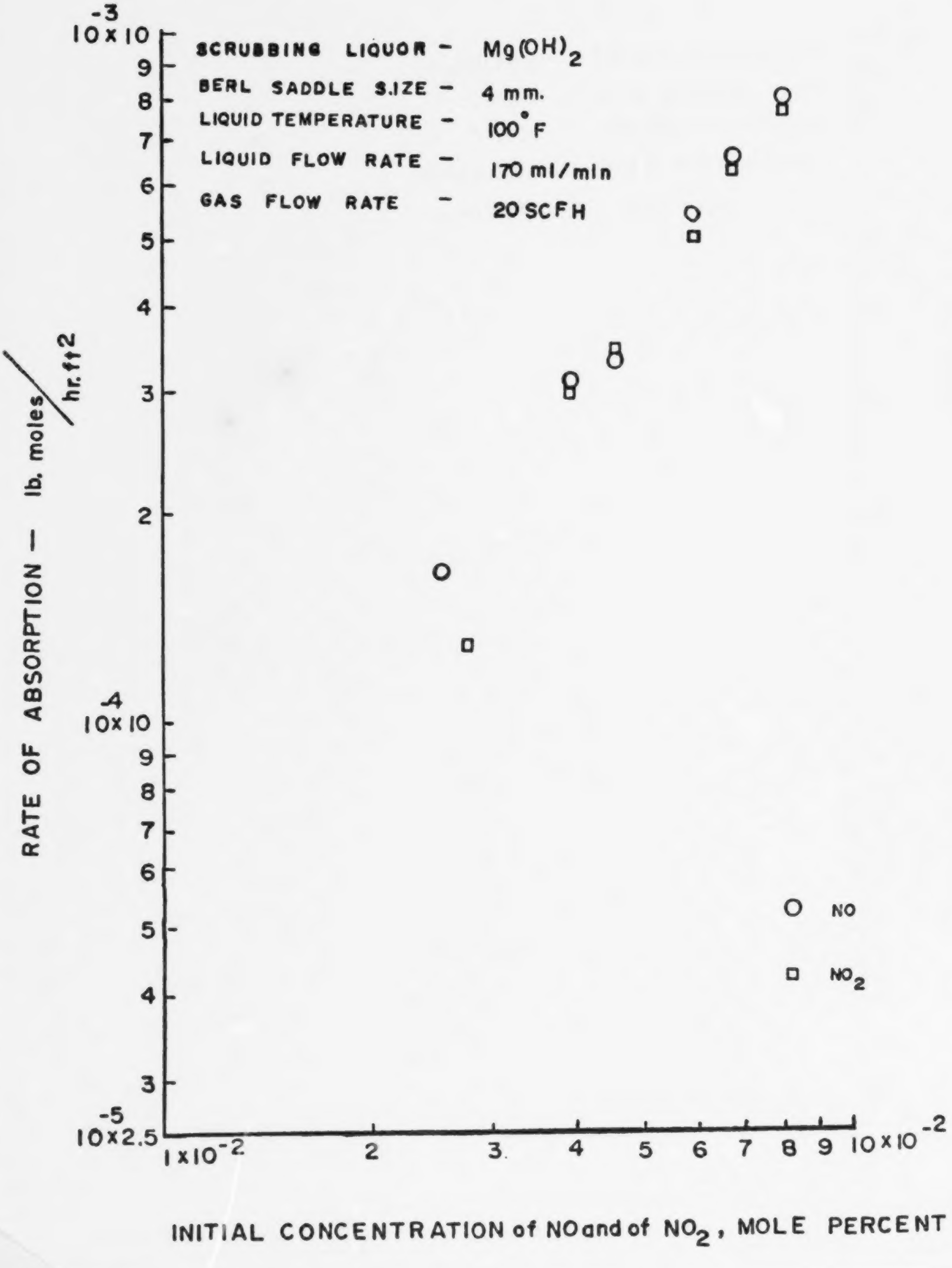


FIGURE 7

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

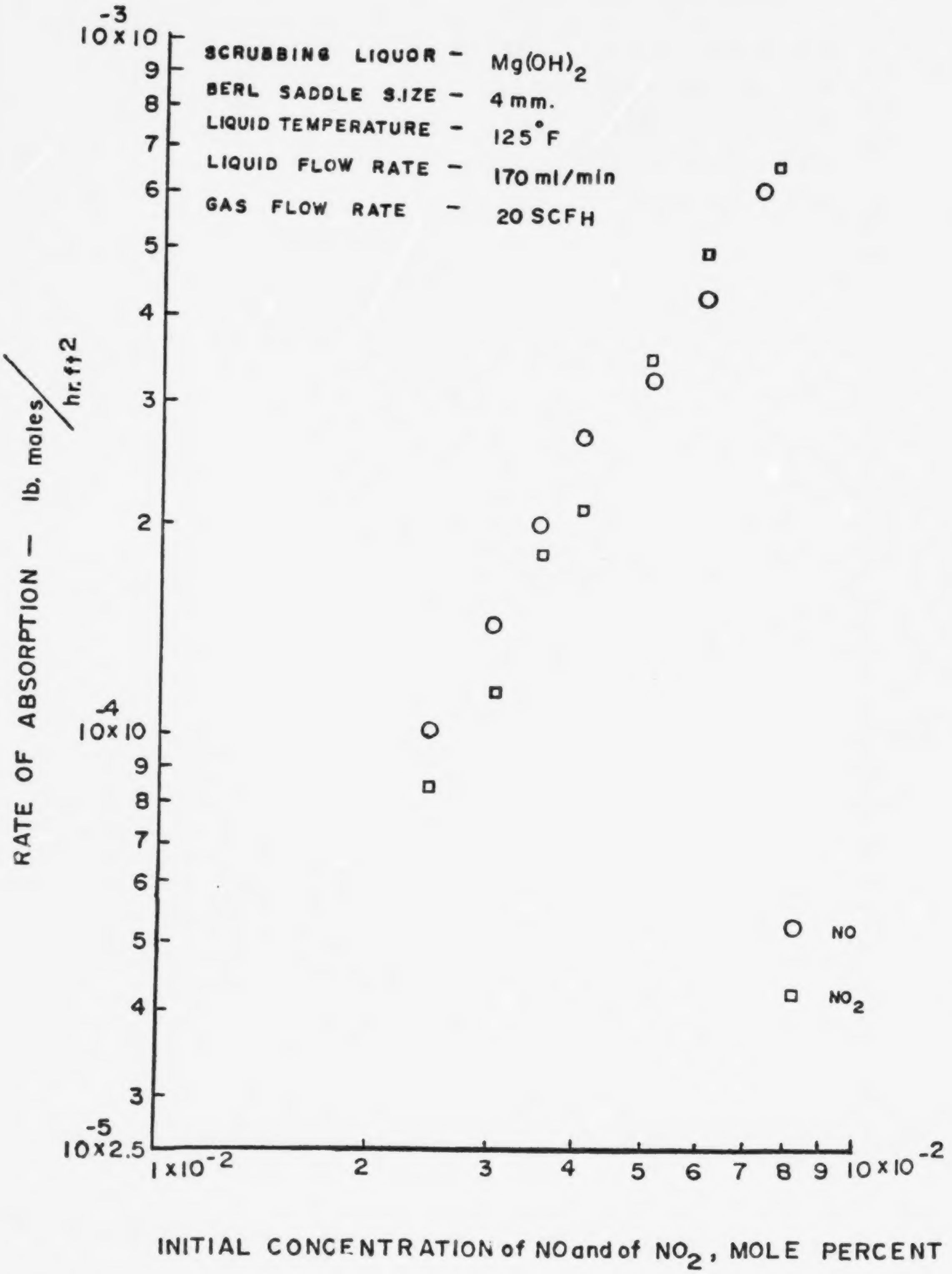


FIGURE 8

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

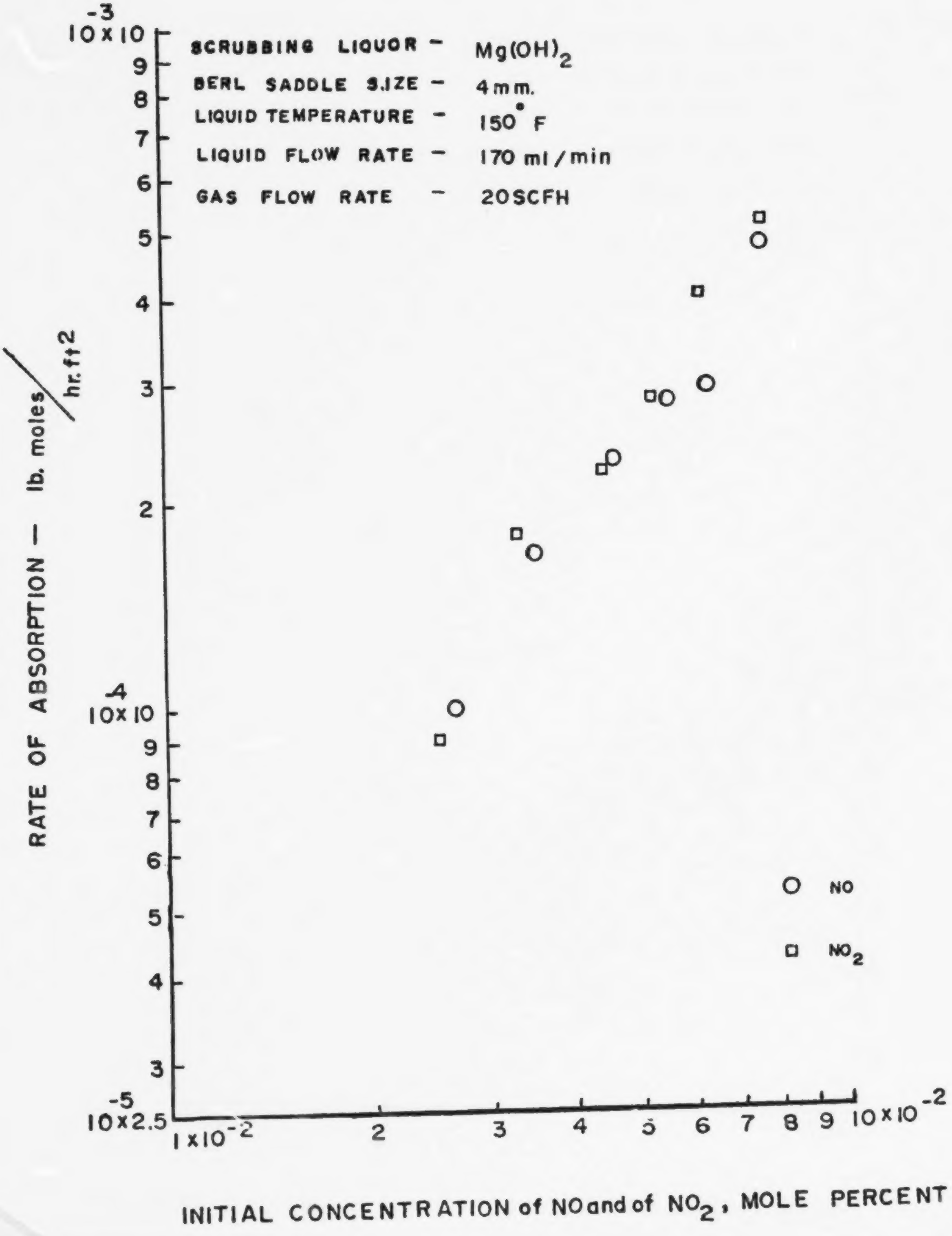


FIGURE 9

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

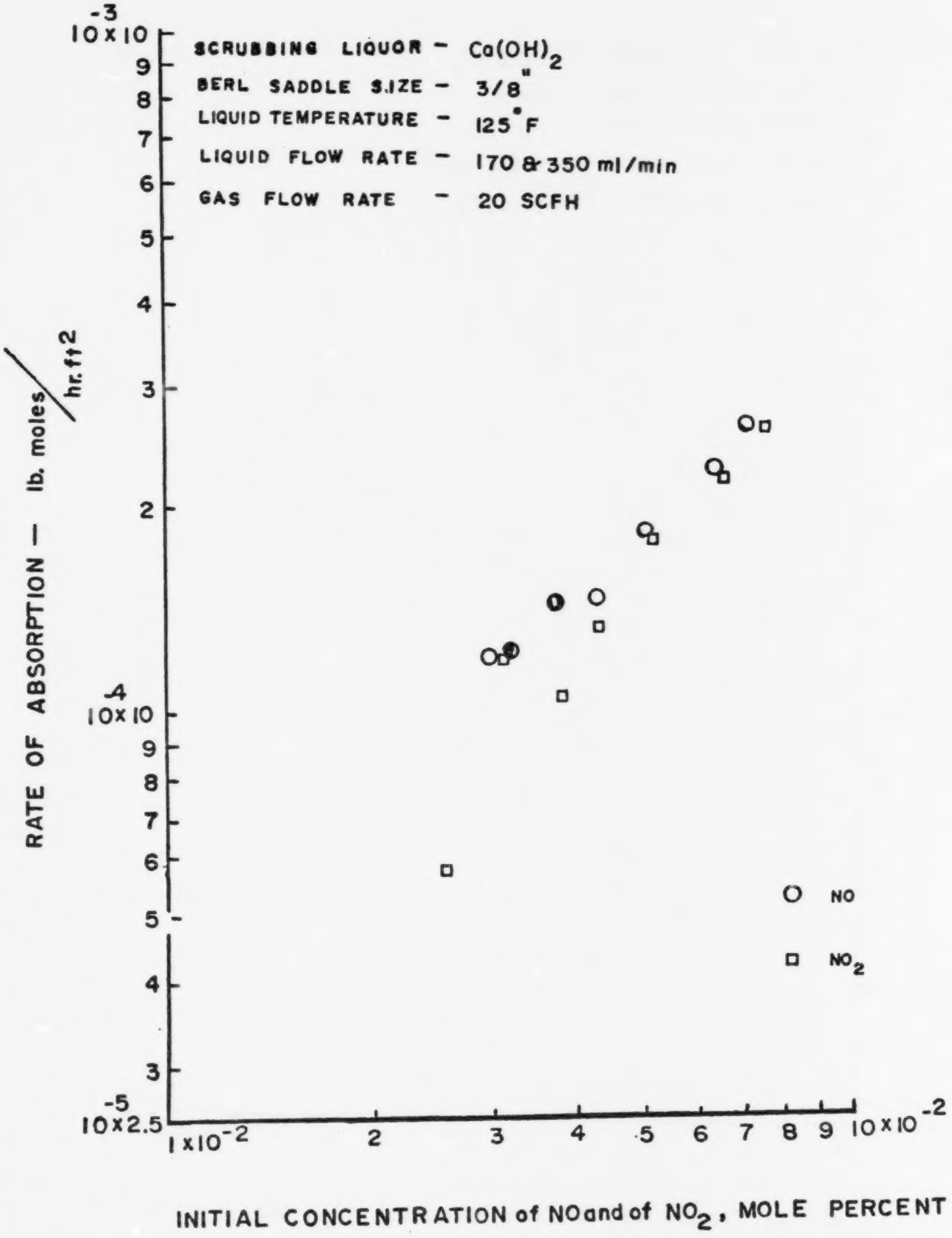


FIGURE 10

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

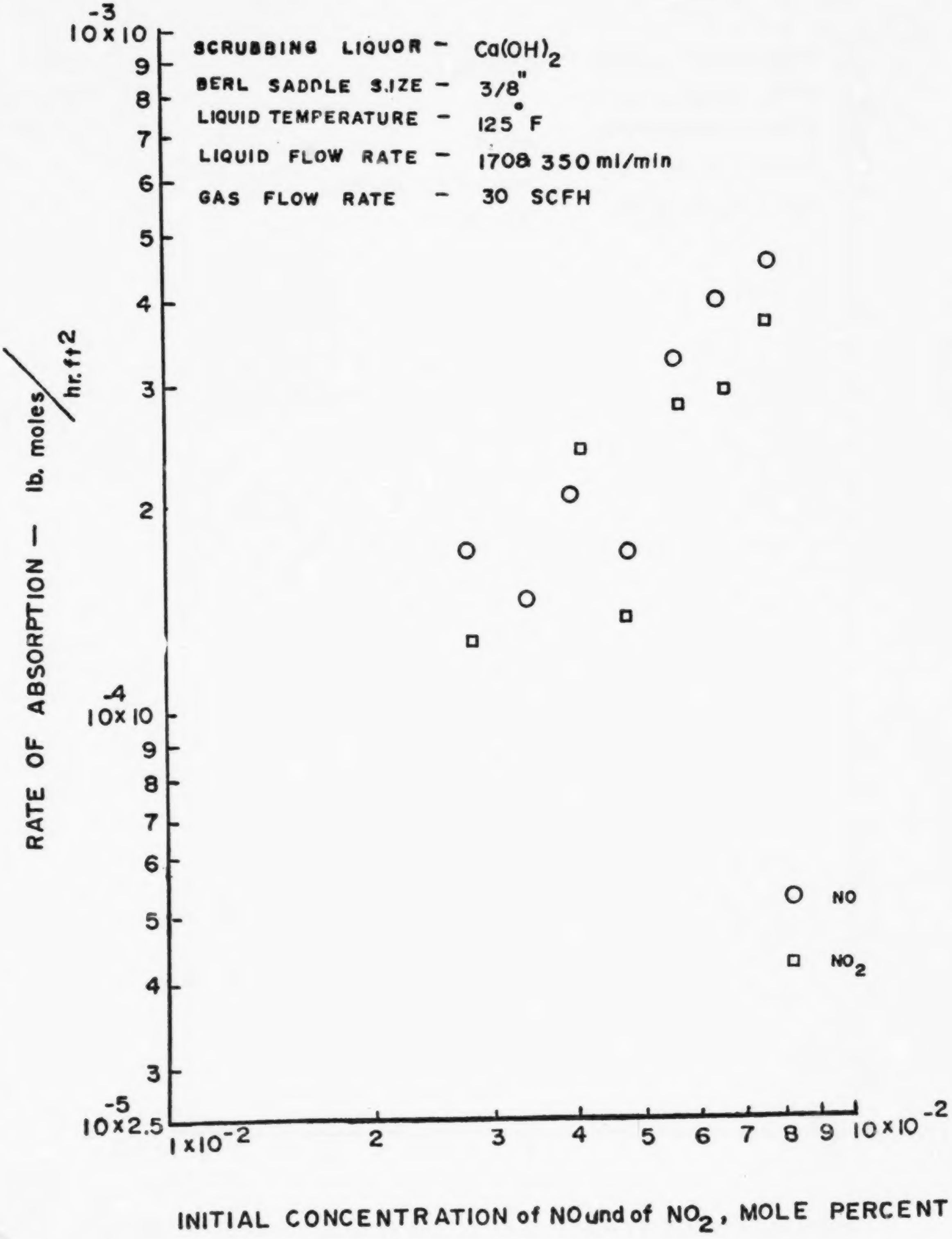


FIGURE 11

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

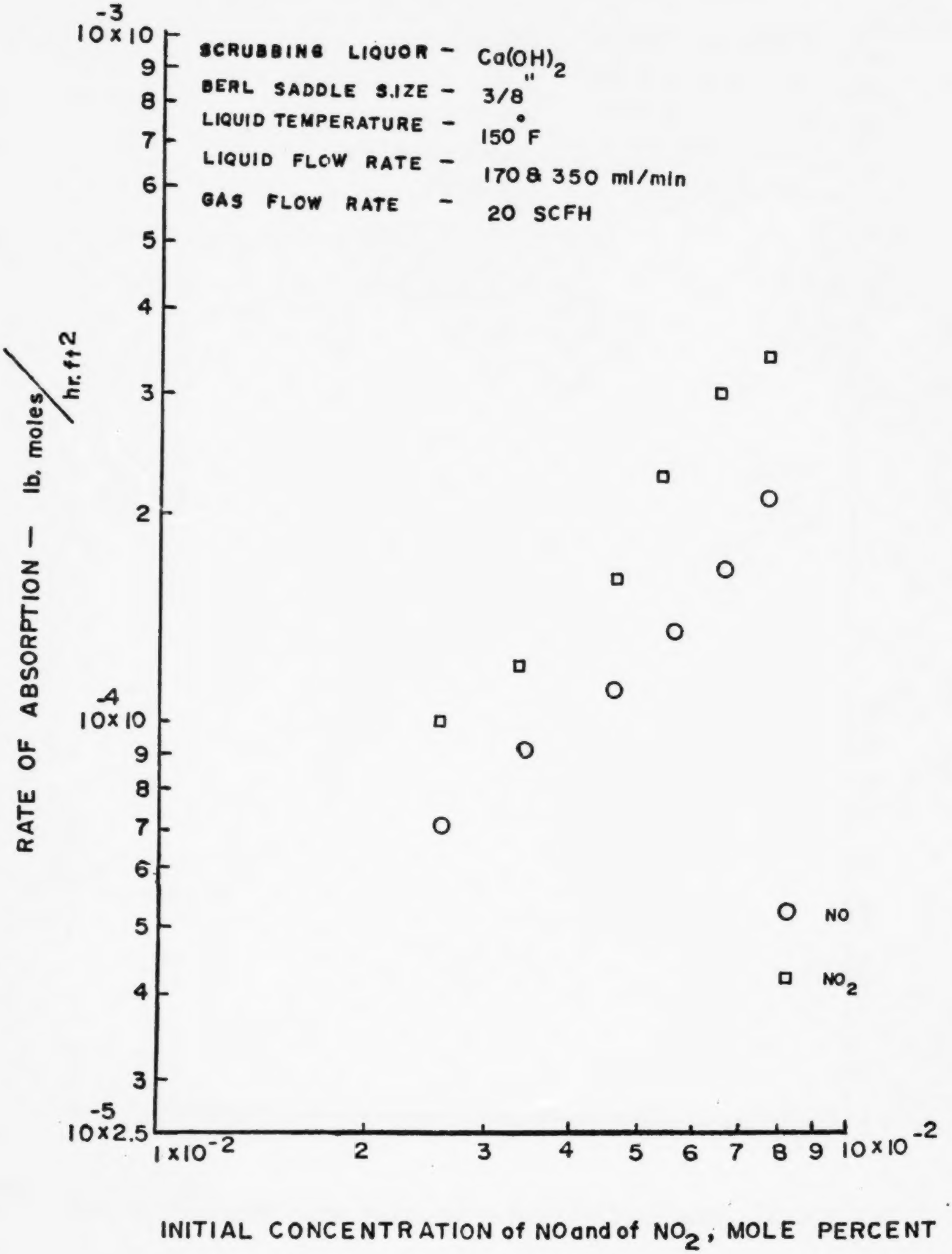


FIGURE 12

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

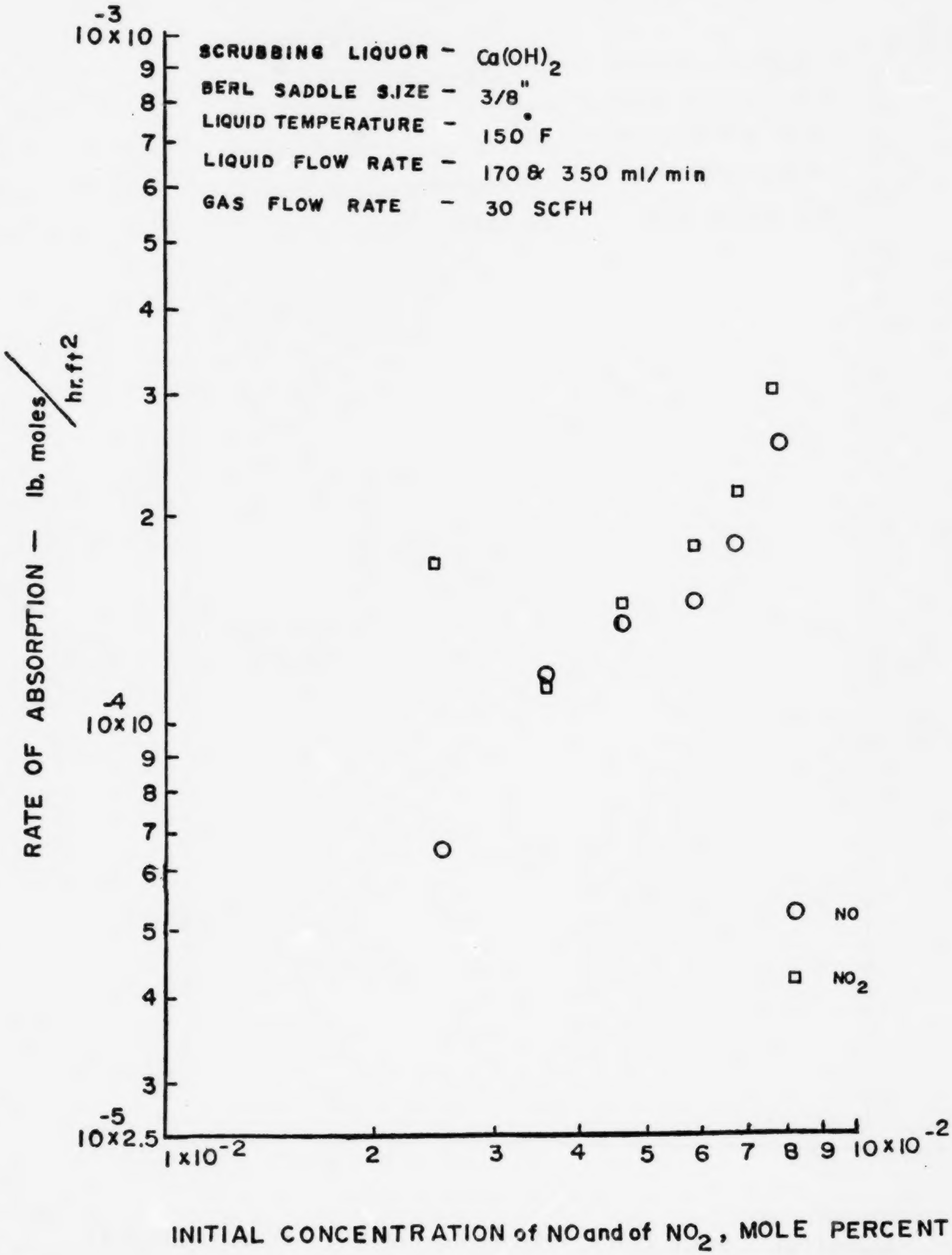
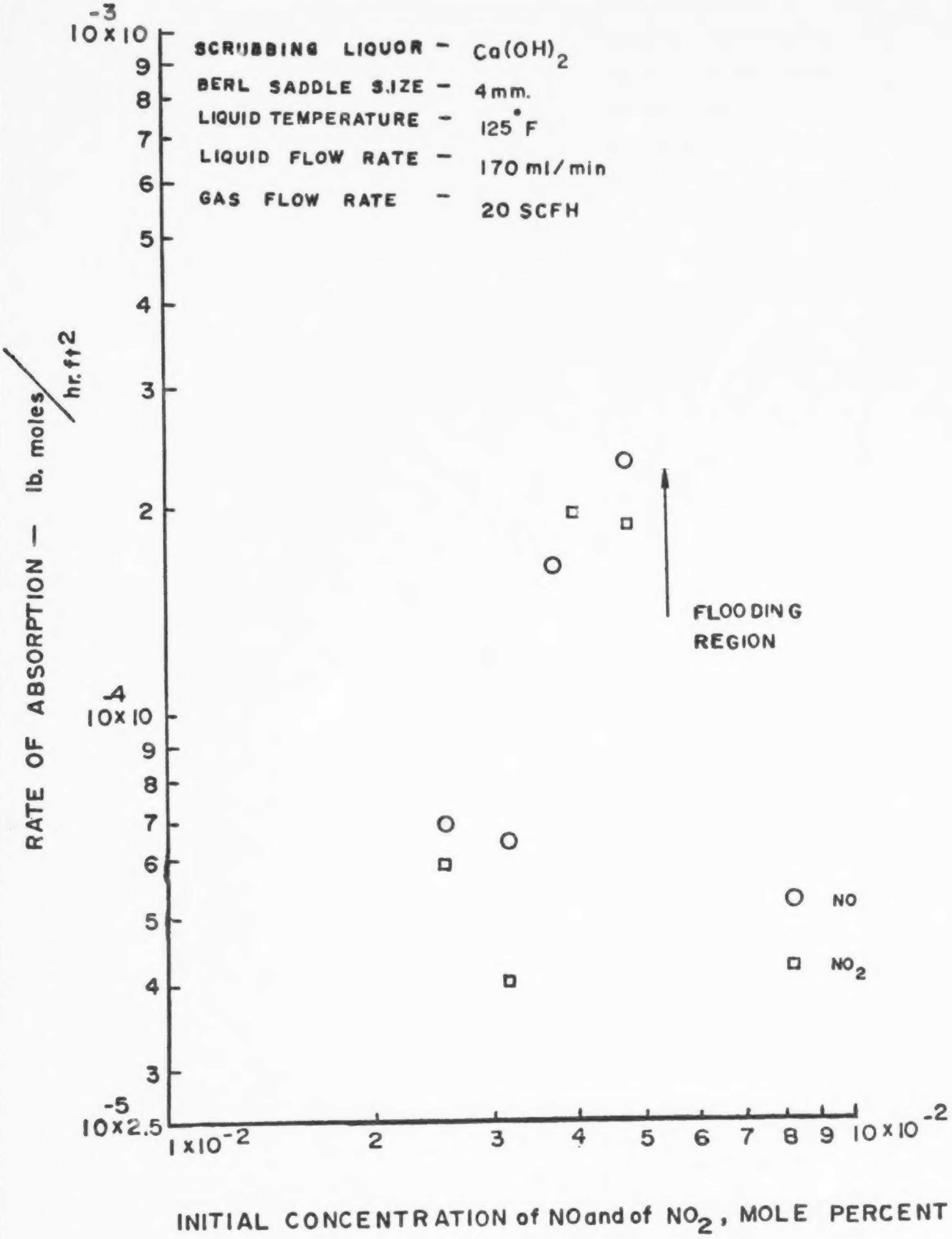


FIGURE 13

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS



The data of Figures 14, 15, and 17 are for runs made with sodium hydroxide. Two concentrations of sodium hydroxide used were 10^{-4} molar and a 5% solution. Comparing these figures, no statistical difference in the rate of absorption of NO and NO_2 relative to changes of temperature, solution or slurry concentration, and packing size were observed.

Figure 16 shows the rate of absorption of NO and NO_2 when a 10^{-4} molar solution of sodium hydroxide is spiked with sodium chloride to 2/3 saturation at the temperature of 125°F. The reason for this run was that the literature quoted the possibility of HNO_3 mist formation during absorption of NO and NO_2. The 2/3 saturated NaCL solution's H_2O vapor pressure is well below that of the inlet gas stream, thus providing a nucleating site for HNO_3 formation. This approach resulted in a small decrease in the rate of absorption of NO and NO_2. The rate of absorption was found to be statistically different (lower) from the rates of absorption using magnesium and calcium hydroxide.

Figure 18 shows the rate of absorption of NO and NO_2 when distilled water is used as the scrubbing agent. One can see that the absorption data are very similar to the other data with the hydroxide solutions.

A statistical analysis of the data (i.e. data of Figures 2 through 18) indicates the following:

(a) The concentration of NO and NO_2 in the flue gas stream significantly affects the rate of absorption; NO and NO_2 at 250 ppm in flue gas is absorbed at a lower rate that 750 ppm NO and NO_2.

(b) The type of hydroxide significantly affects the rate of NO and NO_2 absorption, i.e., NaOH is more effective than $Mg(OH)_2$, $Mg(OH)_2$ is better than $Ca(OH)_2$, $Ca(OH)_2$ is better than water. On this particular point we should like to mention that we believe this notable difference was probably associated with the presence or absence of precipitate formation mentioned previously. Precipitate formation during a run changes the flow patterns and causes channeling which produces changes in the rates of absorption.

(c) Over the ranges employed, changes in slurry or liquid temperature, changes in slurry or liquid flow rates, and changes in packing produced no statistical differences in the absorption of NO and NO_2.

The percentage removals of NO and NO_2 expressed as total NO_x removed (shown in Figures 2 through 18) are as follows for the feed concentration studied:

FIGURE 14

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

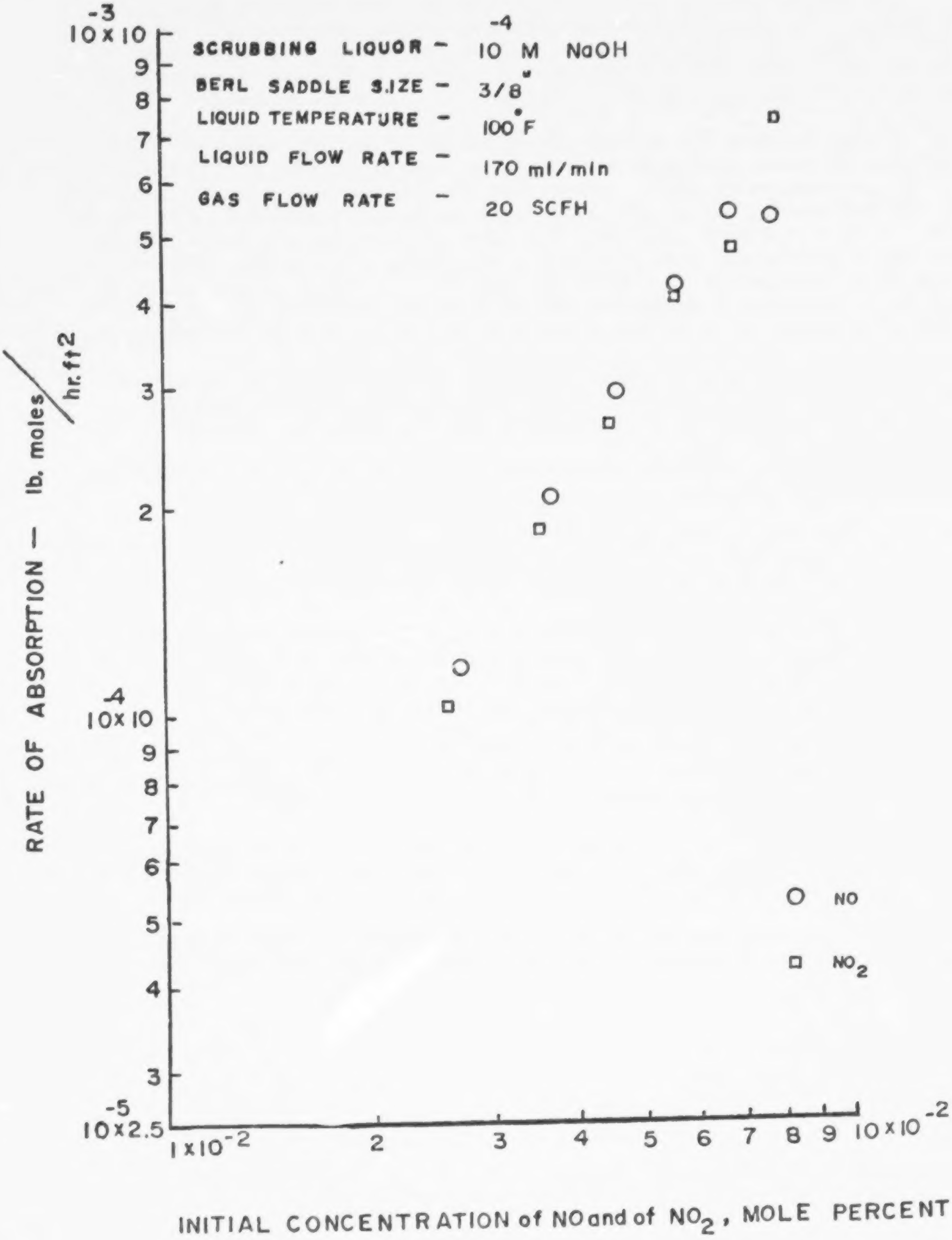


FIGURE 15

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

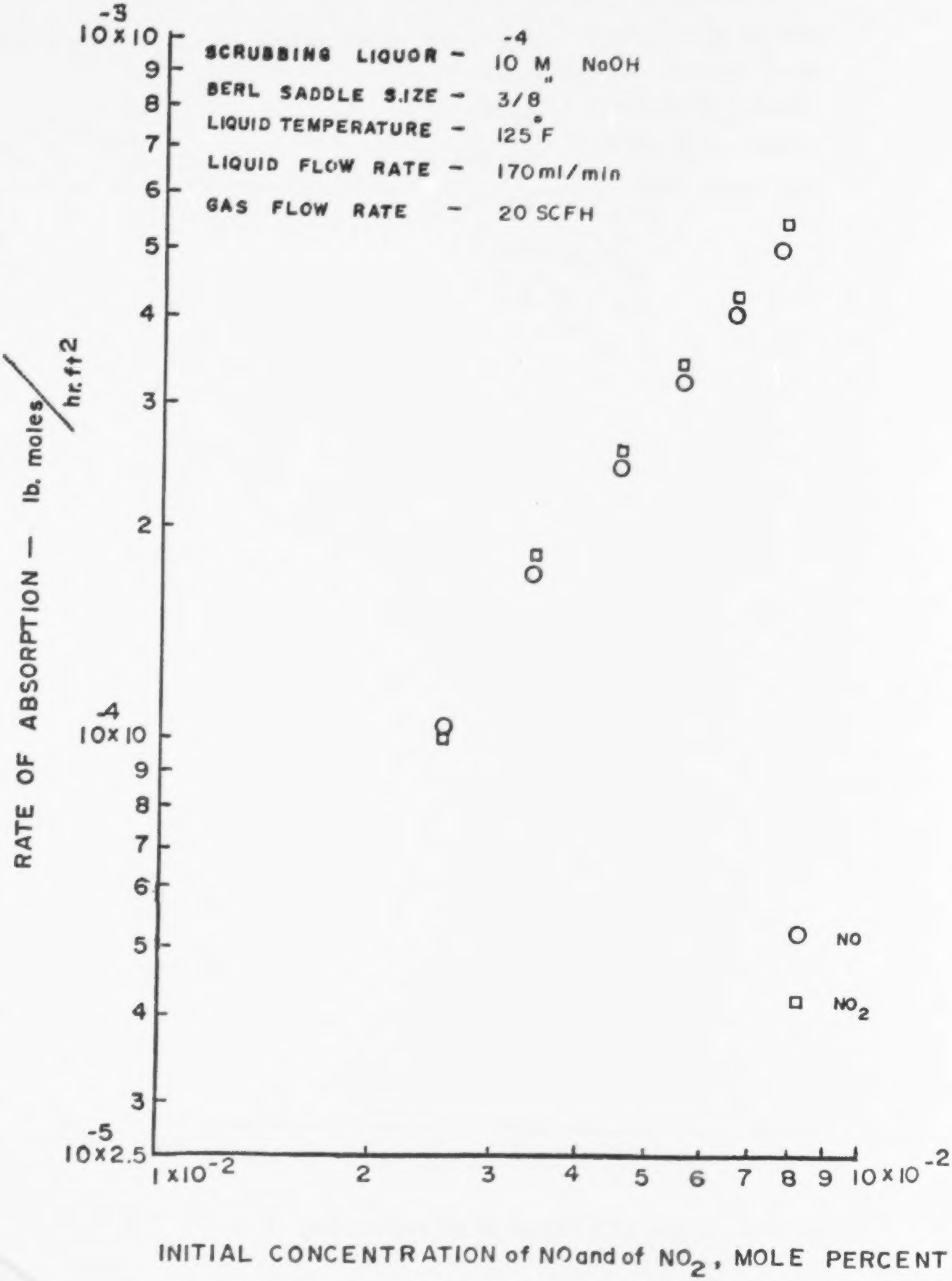


FIGURE 16

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS

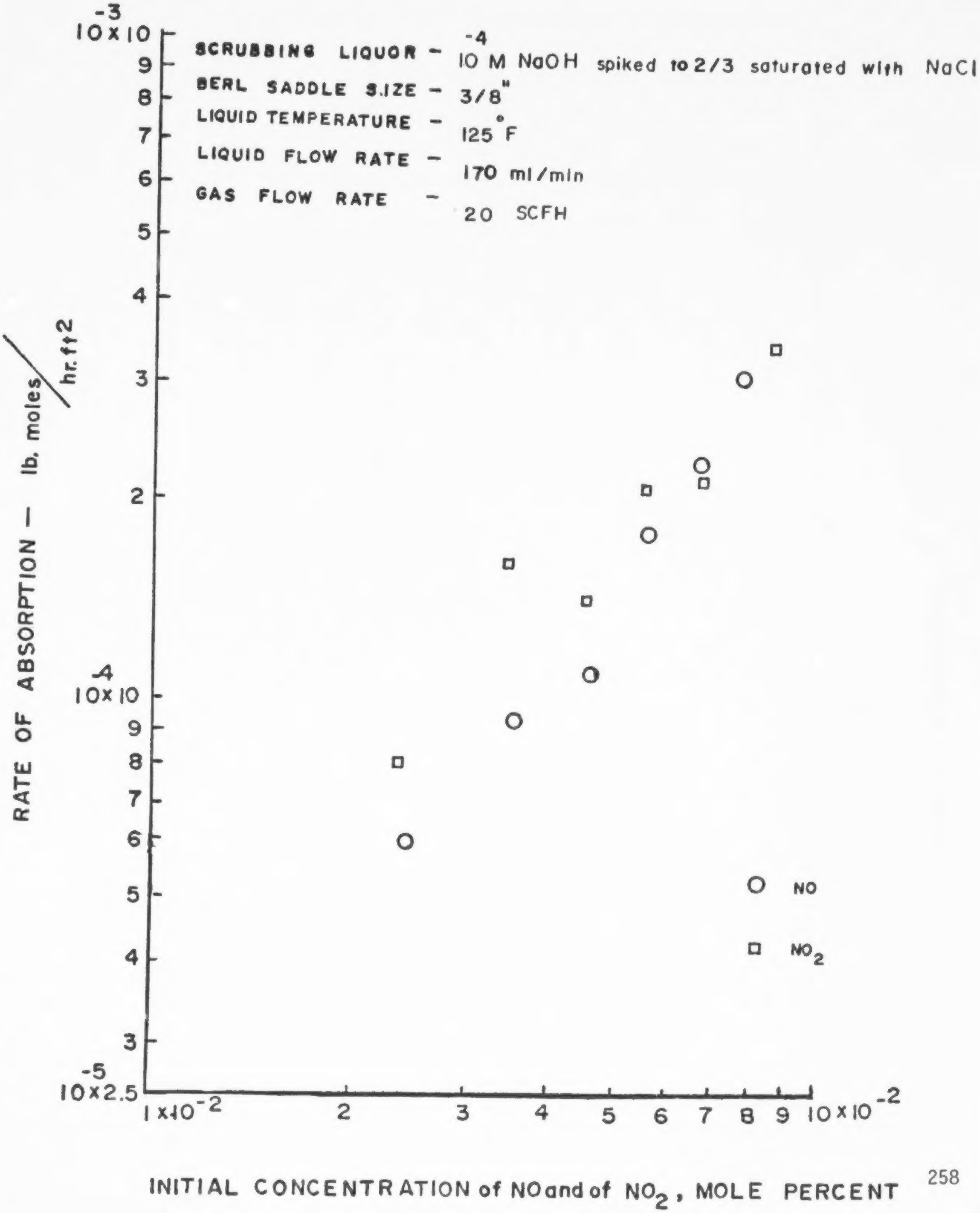
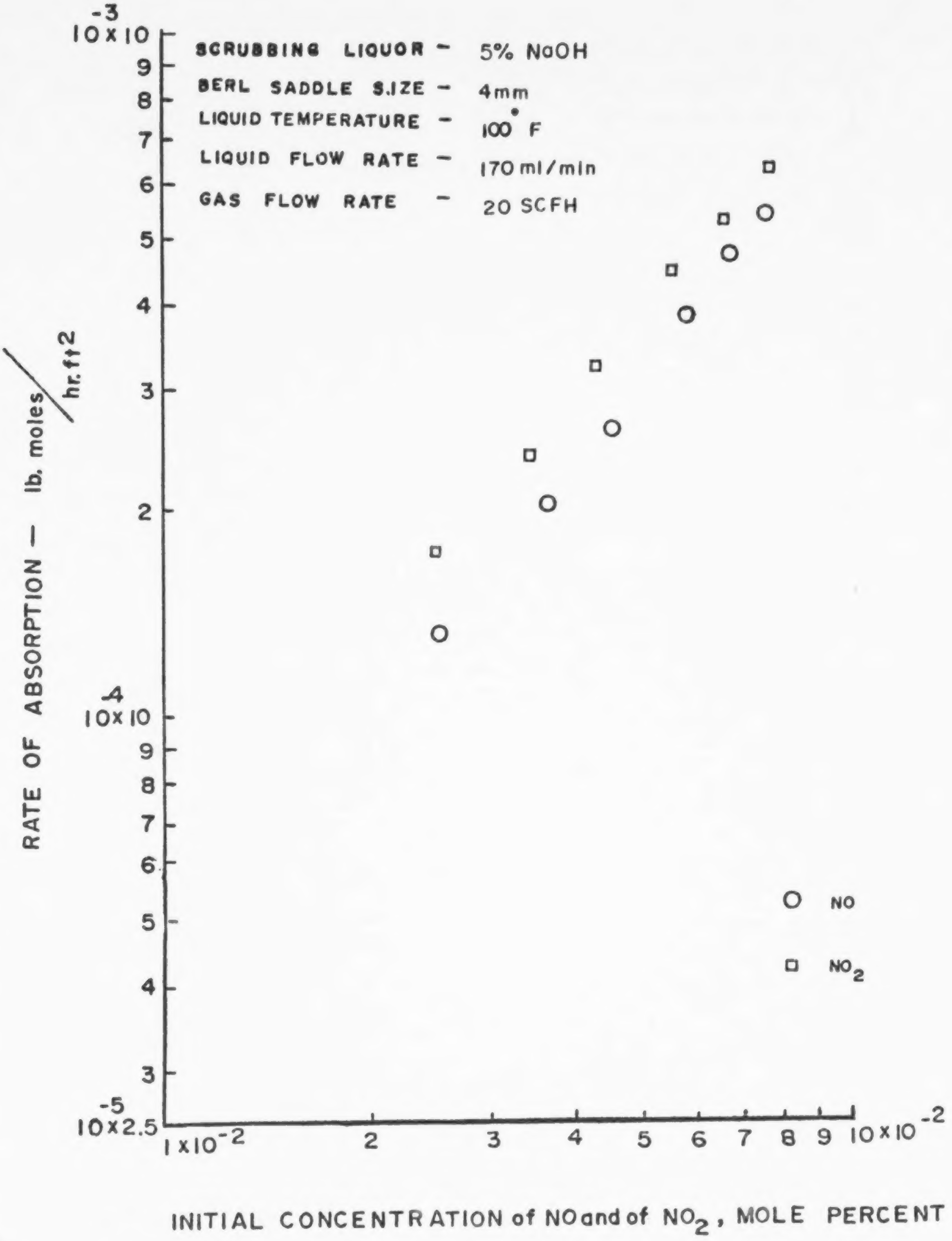


FIGURE 17

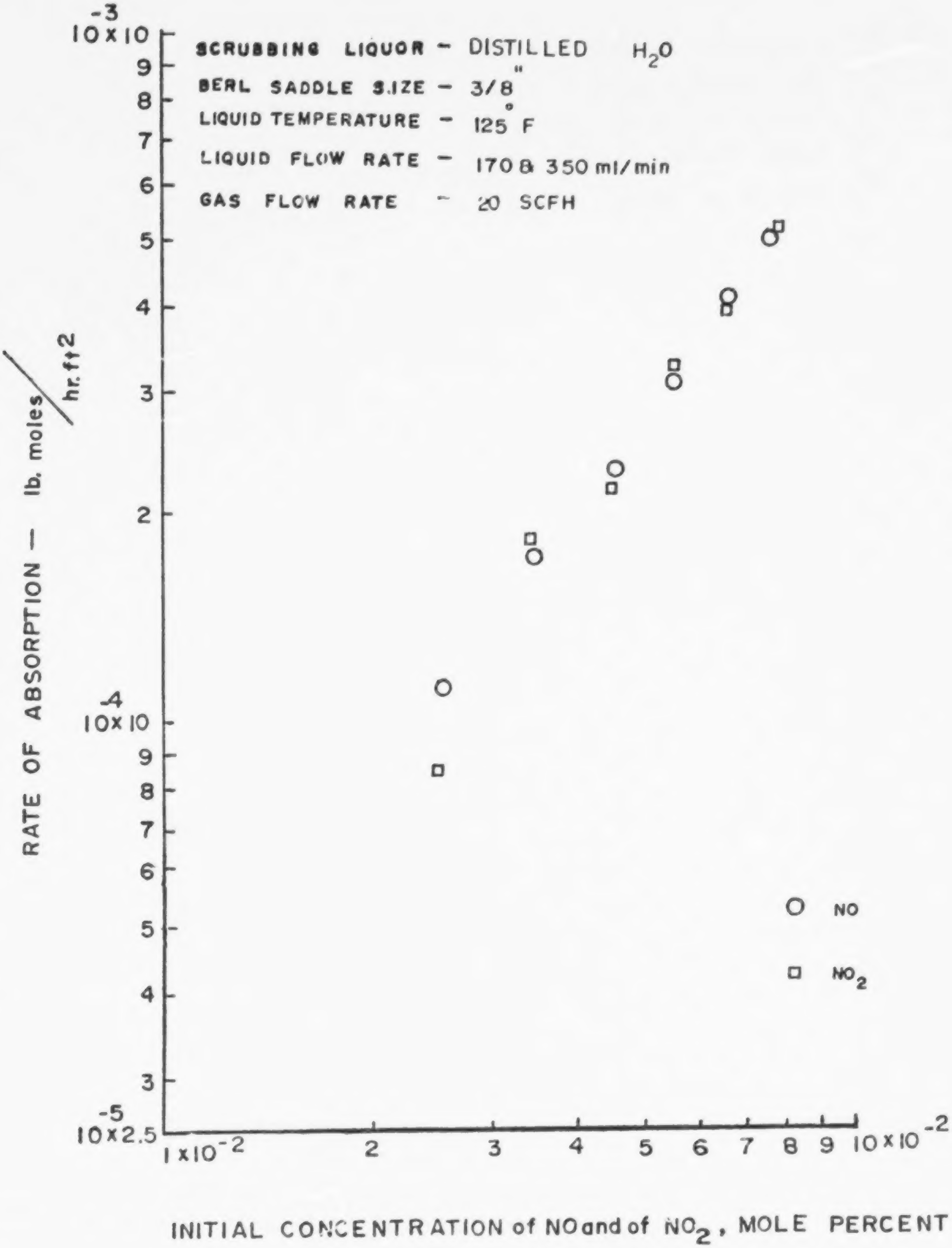
RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS



INITIAL CONCENTRATION of NO and of NO_2, MOLE PERCENT

FIGURE 18

RELATIONSHIP BETWEEN RATE OF AQUEOUS ALKALINE SCRUBBING OF NO AND NO_2 AND INITIAL CONCENTRATIONS OF EQUIMOLAR AMOUNTS IN FLUE GAS



NO and NO_2 Concentration in Flue Gas	% Removal
250 ppm	12 to 14
500 ppm	17 to 19
750 ppm	27 to 29

CONCLUSIONS

The main conclusion drawn at present from our test is that equimolar concentrations of NO and NO_2 in flue gas between 250 ppm and 750 ppm are scrubbed by aqueous solutions of $Ca(OH)_2$, $Mg(OH)_2$, and of NaOH with poor overall scrubbing efficiency. Since no change in absorption was observed due to changes in liquid flow rate, and the large effect of NO_x partial pressure on scrubbing efficiency was found, this may be indicative of gas phase reaction limitations.

A study of the kinetics of the reactions taking place in the gas phase might yield the rate limiting mechanism. Should such a mechanism or mechanisms be found, then steps to catalyze these reactions possibly might improve the alkaline scrubbing efficiency sufficiently to make alkaline scrubbing an acceptable abatement process for low concentrations of equimolar quantities of NO and NO_2.

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REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY:
USE OF ORGANIC ACIDS

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November 8-12, 1971

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ABSTRACT

A survey of weak organic acids showed that many of them are capable of dissolving $CaCO_3$ and $MgCO_3$ and therefore are of potential value in improving the scrubbing of SO_2 by limestone slurries.

The physicochemical properties of four selected acids--benzoic, phthalic, glycolic, and adipic--and their calcium and magnesium salts were determined with respect to stability, solubility, effect on the oxidation rate of sulfite to sulfate, and the nature of aqueous species.

Small-scale tests were made to demonstrate the effectiveness of some of the organic acids in improving absorption of SO_2. The proportion of benzoic acid required to effect an improvement was determined in closed-loop spray tower operation under conditions designed to remove about 50% of the SO_2 without additive. The addition of 10% of the stoichiometric amount of benzoic acid to solubilize the feed limestone increased the SO_2 removal by about 10 percentage points; 50% of the stoichiometric acid gave a 22-percentage point increase, but further improvement with added acid was small. The use of benzoic acid resulted in a higher degree of oxidation of the product solids in the scrubbing operation, although laboratory tests with oxygen indicated that oxidation of dissolved sulfite is inhibited by the acid. The high oxidation in the scrubber tests presumably resulted from the lower pH brought about by the benzoic acid addition and the consequent larger amount of dissolved sulfite available for oxidation.

Organic acids not only improve SO_2 removal but also offer the opportunity of getting complete utilization of limestone by using enough acid to dissolve all the feed limestone, in which case the only solid phases are calcium sulfite and sulfate. The increased oxidation in the scrubber should also improve slurry settling rate and avoid the danger of limestone surface blinding. Work on these possibilities is continuing.

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY: USE OF ORGANIC ACIDS

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The dissolution of limestone is one of the limiting reactions in the removal of sulfur dioxide from stack gases by scrubbing with a limestone slurry. The equilibrium solubility of limestone in water (Table I) does not give a great driving force to effect solution; consequently, it has been found advantageous to have a surge vessel to permit dissolution of limestone and precipitation of calcium sulfite - sulfate before sending the slurry to the scrubber. The low concentration of basic components in the solution also necessitates a higher ratio of liquid to gas (L/G) in the scrubber than is required for other scrubbing agents such as alkali metal salts or ammonia.

TABLE I

Solubility of $CaCO_3$ in Water at 50°C (122°F)[a]

Ca ppm	P_{CO_2} atm	pH
9.5	0.000136	8.5
16.8	0.000803	8.0
30.7	0.00466	7.5
57.7	0.0271	7.0
111.1	0.159	6.5
221.7	0.950	6.0
1020.3	36.3	5.0

[a] Calculated using Radian's equilibrium program (PB 193029) for the system $CaO-CO_2-H_2O$.

The solubility of limestone increases rapidly with decrease in pH as shown in Table I. A similar increase can be achieved by adding another acid, provided that:

(1) the calcium salt of the added acid is soluble, and

(2) the ionization constant of the added acid is greater than that of carbonic acid, H_2CO_3 ($K_1 = 4.4 \times 10^{-7}$)

By stipulating also that the added acid be weaker than sulfurous acid, H_2SO_3 ($K_1 = 1.3 \times 10^{-2}$), the limestone slurry scrubbing of stack gases might well be improved significantly by the addition of a small amount of an extraneous acid (an acid stronger than H_2SO_3 would volatilize SO_2 from solution and prevent its precipitation as the calcium salt).

This paper describes a survey of possible acid additives, laboratory tests of properties of selected acids and their salts, and small-scale tests of selected additives to determine their effectiveness in SO_2 removal and other operational characteristics.

Survey of Acids and Exploratory Tests

Of the 132 acids (intermediate in strength to H_2SO_3 and H_2CO_3) that are listed in chemical handbooks, many are organic acids whose physicochemical properties in aqueous systems have not been studied. Many can be eliminated from consideration as additives to limestone slurries because of cost or difficulty to produce; others are of too high molecular weight to be soluble in water; and others, such as oxalic acid, have extremely insoluble calcium salts. The ideal additive would be

(1) soluble in water and limestone scrubber slurry;

(2) nonvolatile and stable under scrubbing conditions;

(3) not precipitated by Ca, Mg, or other metals likely to be found in the solution; and

(4) commercially available and of reasonable cost.

Solubility of Carbonates at 25°C: Measurements were made of the ability of several organic acids to dissolve calcium carbonate and magnesium carbonate at room temperature (~78°F). The acids were those available in our laboratory at the time and consisted of both aliphatic and aromatic acids (monobasic and polybasic) and covered a wide range in molecular weight. The procedure consisted in adding 1 gram of the organic acid (or 1 ml if the acid was a liquid) to 100 ml of water and then adding 5 grams of reagent $CaCO_3$ or $MgCO_3$ to the solution or mixture. The mixtures were allowed to stand for 1 week with occasional agitation by hand to promote dissolution. Aliquots of 10 ml of the clear solution were taken after 3 days and after 1 week from each mixture and were analyzed for the dissolved metal. The pH was measured before addition of the carbonate and after the 7-day sample. The results are presented in Table II.

TABLE II

Use of Organic Acids in the Dissolution of Calcium and Magnesium Carbonates

Acid	Formula	pH of acid solution	Sol., Ca, wt. %, after		After 7 days		Sol., Mg, wt. %, after		After 7 days		Price dollars/lb.
			3 days	7 days	mole ratio acid:Ca[b]	pH	3 days	7 days	mole ratio acid:Mg[b]	pH	
Aliphatic monocarboxylic acids											
Formic	$HCOOH$	2.30	0.48	0.54	1.7	7.00	0.40	0.41	1.4	7.60	0.147
Acetic	CH_3COOH	2.30	0.32	0.37	1.9	7.20	0.31	0.31	1.4	7.65	0.09
Chloroacetic	$ClCH_2COOH$	2.15	0.21	0.21	2.0	7.15	0.20	0.20	1.3	7.85	0.21
Glycolic	$HOCH_2COOH$	2.40	0.22	0.25	2.1	7.40	0.24	0.27	1.2	7.50	0.10
Phenylacetic	$C_2H_5CH_2COOH$	2.70	0.13	0.15	2.0	7.40	0.14	0.13	1.4	8.15	0.68
Propionic	C_2H_5COOH	2.90	0.28	0.28	1.9	7.20	0.27	0.21	1.6	7.75	0.147
Lactic	$CH_3CHOHCOOH$	2.50	0.21	0.23	1.9	6.90	0.21	0.21	1.3	7.70	0.275
Butyric	C_3H_7COOH	2.90	0.22	0.21	2.2	6.65	0.23	0.21	1.3	7.50	0.33
Caproic	$C_5H_{11}COOH$	3.00	0.17	0.17	2.0	6.15	0.15	0.12	1.7	7.90	
Gluconic	$CH_2OH(CHOH)_4$ $COOH$	2.80[a]	0.06	0.06	3.4	7.00	0.06	0.08	1.6	8.00	0.145
Acrylic	$CH_2=CHCOOH$	2.60	0.31	0.31	1.8	6.60	0.25	0.21	1.6	7.70	0.31
Oleic	$CH_3(CH_2)_7C=C$ $(CH_2)_7COOH$	3.80[a]	0.01	0.01	16.7	6.60	0.03	0.03	3.4	8.45	0.23
Aliphatic polycarboxylic acids											
Oxalic	$COOHCOOH$	1.75	0.01	0.01	44.4	7.70	0.13	0.08	3.4	8.35	0.22
Succinic	$COOHCH_2CH_2COOH$	2.30	0.27	0.32	1.1	7.35	0.29	0.30	0.69	7.80	0.62
Tartaric	$COOHCHOHCHOH$ $COOH$	2.25	0.01	0.01	26.7	7.70	0.24	0.26	0.62	7.85	0.415
Malic	$COOHCHOHCH_2COOH$	2.40[a]	0.09	0.09	3.3	7.60	0.22	0.24	0.76	8.40	0.315
Fumaric	$COOHCH=CHCOOH$	2.35[a]	0.25	0.28	1.2	7.30	0.28	0.27	0.78	8.00	0.225
Maleic	$HO_2CCH=CHCO_2H$	1.95	0.23	0.31	1.1	7.25	0.31	0.30	0.70	7.70	0.48
Adipic	$COOH(CH_2)_4COOH$	2.80	0.28	0.28	1.0	7.20	0.26	0.21	0.79	7.80	0.18
Citric	$(COOHCH_2)_2OOH$ $COOH$	2.25	0.02	0.02	10.	7.80	0.24	0.24	0.53	8.50	0.33
Aromatic acids											
Benzoic	C_6H_5COOH	2.75[a]	0.14	0.17	1.9	7.35	0.04	0.13	1.5	8.20	0.215
Salicylic	HOC_6H_4COOH	2.60[a]	0.11	0.14	2.1	7.35	0.21	0.13	1.4	8.15	0.425
P-Amino benzoic	$NH_2C_6H_6COOH$	3.50[a]	0.15	0.15	1.9	7.40	0.14	0.14	1.3	8.00	1.72
Dinitro benzoic	$(NO_2)_2C_6H_3$ $COOH$	2.80[a]	0.09	0.10	1.9	7.45	0.09	0.09	1.3	8.10	
Gallic	$(HO)_3C_6H_7$ $COOH$	2.85	0.11	0.11	2.1	6.20	0.12	0.11	1.3	8.15	2.65
Phthalic	$C_6H_6(COOH)_2$	2.45[a]	0.12	0.06	4.0	7.60	0.22	0.21	0.70	8.05	0.12
α-Naphthoic	$C_{10}H_7COOH$	3.75[a]	0.02	0.01	23	6.70	0.08	0.06	2.3	8.30	

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[a] 1 gram of acid did not completely dissolve in 100 ml. H_2O.

[b] Based on solubilities after 1 week, assuming all acid dissolved.

The pH of the acid solutions varied from 1.75 to 3.80 (many of the higher molecular weight acids did not completely dissolve before the carbonate addition). The pH of the final solutions or slurries ranged from 6.2 to 7.8 for $CaCO_3$ and from 7.5 to 8.5 for $MgCO_3$.

Most of the mixtures dissolved very little after the third day. The Ca-Mg content of a few samples actually appeared to decrease between 3 and 7 days. Some of these variations may be due to sampling and analytical errors, while others may be real. Despite the apparent lack of equilibrium in many of the mixtures, the final mole ratios (acid:metal) shown in Table 2 are indicative of the potential of the acid to dissolve the carbonate. For the monobasic acids of appreciable solubilizing power, this ratio was approximately 2 for Ca and 1.5 for Mg; for the dibasic acids, the corresponding ratios were 1 and 0.75. The results indicate that those acids having a solubilization ratio of 2-COOH groups per atom of Ca should be considered as potential limestone slurry additives as this is the stoichiometric value.

The data in Table II also show that the low molecular weight acids were more effective in solubilizing calcium or magnesium carbonate per gram of acid than were the high molecular weight acids. This is due to (1) more carboxy groups per gram and (2) increased solubility of the low molecular weight acids in water. The substitution of chlorine, hydroxy, or phenyl groups for hydrogen decreased the solubilizing power per gram as expected, while acids whose calcium salt is insoluble were particularly ineffective (e.g., oxalic, tartaric, and citric acids).

Batch Exploratory Tests: Laboratory tests in batch apparatus were conducted to compare the effectiveness of various organic acids in improving scrubbing efficiency and limestone utilization. The tests were made by adding the acid to 1% limestone slurry and using the mixture to scrub a synthetic flue gas, with stirring, in a gas scrubber bottle. The SO_2 content of the gas, before and after scrubbing, was monitored by an infrared analyzer. The SO_2 removals and CaO utilizations were calculated by two methods, one based on chemical analyses of the spent scrubber liquor and the other on evaluation of the infrared recorder chart; the latter method appeared to be more reliable. The acids tested were salicylic, citric, formic, benzoic, and acetic. The results are presented in Table III.

Although the data are somewhat scattered, there is an indication that salicylic and citric acids caused a decrease in the utilization of limestone; citric acid, at very low concentration (acid: CaO mole ratio = 0.06), appeared to have no deleterious effect. Formic, benzoic, and acetic acids increased the utilization of limestone, the overall SO_2 recovery, and the time to 50% removal. Reasons for the poor performance of salicylic and citric acids may be the high value of the ionization constant, the low solubility of salicylic acid, and the ineffectiveness of citric acid in dissolving $CaCO_3$ (Table II). Formic and acetic acids are quite volatile and could result in substantial losses in scrubbing a stack gas.

TABLE III

Laboratory-Scale Batch Tests of the Use of Weak Organic Acids

Test No.	326	364	338	341	335	339	333	342	343	340	332
Acid added											
Type	None	Salicylic	Citric			Formic		Benzoic		Acetic	
Ionization constant[a]	-	1.06×10^{-3}	8.4×10^{-4}			1.76×10^{-4}		6.3×10^{-5}		1.75×10^{-5}	
Amount added											
Grams	-	1.0	2.1	1.0	0.1	1.0		2.2	0.2	1.0	
Moles x 10^3	-	7.2	10.9	5.2	0.5	21.7		18.0	1.6	16.7	
Limestone fed[b]											
Grams	1.0	1.0	1.0	1.0	1.0	1.0		1.0	1.0	1.0	
Moles CaO x 10^3	9.2	9.2	9.2	9.2	9.2	9.2		9.2	9.2	9.2	
Water fed, g.	100	99	100	99	99.9	99		97.8	99.8	99	
Scrubber conditions											
Gas rate, l./min.[c]	4.375	3.826	4.273	4.253	4.743	4.273	4.743	4.253	4.253	4.253	4.743
Solution temperature, °F.	121-138	120-125	110-119	122-124	120-125	121-125	118-120	123-126	120-125	120-125	116-125
Total SO_2 fed											
Grams	0.675	0.620	0.509	0.443	0.686	0.775	0.775	0.731	0.731	0.797	0.775
Moles x 10^3	10.5	9.7	7.9	6.9	10.7	12.1	12.1	11.4	11.4	12.4	12.1
Test results											
Maximum SO_2 removal, %[d]	84	81	88	83	87	88	92	88	86	88	93
Time to 50% removal, min.	20	21	15	13	20	23	21	22	22	24	21
Scrubber solution pH	3.1	4.2	3.8	3.9	4.2	4.0	3.7	4.5	4.2	3.9	3.7
Overall SO_2 removal, %											
By chemical analysis[e]	82		56	83	88	86	104	69	67	58	105
By infrared analysis[f]	65	64	75	74	73	75	77	65	73	76	76
CaO utilization based on SO_2 removal, %[g]											
By chemical analysis	94		48	62	102	113	137	85	83	78	138
By infrared analysis	74	67	64	55	85	99	101	80	90	102	100
CaO utilization attributable to acid addition, %[h]											
By chemical analysis	-		-46	-32	8	19	43	-9	-11	-16	44
By infrared analysis	-	-7	-10	-19	11	25	27	6	16	28	26

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[a] First hydrogen ion at 25° C.; value for H_2SO_3 is 1.7×10^{-2} at 25° C., for H_2CO_3 is 3.5×10^{-7} at 18° C. (Handbook of Chemistry and Physics, 21st Edition, Chemical Rubber Publishing Co.)

[b] Crushed (72% -200 mesh) Spring Valley limestone; 51.5% CaO, 1.3% MgO, 41.1% CO_2, 4% SiO_2, 0.05% S.

[c] Simulated flue gas; 0.3% SO_2, 3.5% O_2, 80.2% N, 16.0% CO_2 (dry basis).

[d] Maximum proportion removed as indicated by infrared analysis.

[e] By material balance.

[f] By integration of recorder chart.

[g] 100 (moles SO_2 removed)/(moles CaO input).

[h] (CaO utilization with acid) - (CaO utilization without acid).

Continuous Exploratory Tests: Exploratory tests with citric, formic, benzoic and acetic acids were carried out in a small pilot plant consisting of two unpacked spray towers in series with the recirculating slurry impinging on a deflector plate to give a flat spray. Each scrubber was 4 inches in diameter by 2 feet long. The slurry of 1% limestone was recycled at 9 l/min to scrub about 5 cfm ($L/G = \sim 400$) of simulated flue gas. The procedure in these tests was to start with fresh slurry in the surge tanks and adjust system flows and conditions to give maximum removal of SO_2. Operation was carried out without slurry addition until removal started falling off, and then a flow of fresh slurry was started in an open-loop manner; the slurry flow rate was varied as necessary to maintain SO_2 removal at approximately the initial level. Each test represents about 5 hours of steady-state operation. The amount of acid added was 10% of the stoichiometric amount for reaction with the limestone feed. The results and conditions are presented in Table IV.

Citric acid gave better removal at 10% stoichiometric addition than did the control test, but utilization of limestone was poor and a high feed rate of makeup slurry was required to maintain SO_2 removal; increasing the citric acid to 50% of the stoichiometric limestone feed gave even worse results. Formic, benzoic, and acetic acids were more effective; the SO_2 removal and limestone utilization were higher at lower makeup feed rate. When the supernatant liquid from a previous acetate run (No. 64) was used to slurry the limestone, the results were poorer, indicating a possible loss of acetic acid due to volatilization.

The product solids contained a much higher proportion of sulfate in those tests in which organic additives gave increased utilization of the limestone and improvement in SO_2 removal. Since sulfate crystals are larger than sulfite, this phenomenon may improve the settling rate of the slurry in waste ponds; it may also reduce the possibility of sulfite pollution if there is seepage into ground water or streams from the pond.

Physicochemical Properties of Four Selected Acids

Four acids were chosen from the exploratory tests to determine their properties (and those of their Ca and Mg salts) that are important to use in limestone slurry scrubbing.

	Aliphatic	Aromatic
Monobasic	Glycolic, $CH_2OHCOOH$	Benzoic, C_6H_5COOH
Dibasic	Adipic, $HOOC(CH_2)_4COOH$	Phthalic, $C_6H_4(COOH)_2$

These were selected on the basis of potential stability and nonvolatility, ability to solubilize $CaCO_3$ and $MgCO_3$ (Table II) and their commercial availability at a reasonable price.

TABLE IV

Effect of Weak Acid Type in Increasing Solubility of Limestone Used in Scrubbing Stack Gas[a]

Acid Additive[c]	Chalk	Limestone[b]						
	None	None	Citric	Citric[d]	Formic	Benzoic	Acetic	Acetic[e]
Test No.[f]	66	63	67	69	61	70	64	65
Makeup slurry feed rate,[g] l./hr.	16.5	20.6	19.8	21.7	14.0	8.0	12.6	18.0
Stack gas[h]								
Inlet temperature, °F.	300	305	305	302	300	304	310	295
SO_2 content, p.p.m.								
To first-stage scrubber	3395	3200	3290	3255	3300	3235	3450	3450
From second-stage scrubber	410	615	290	730	380	305	395	520
Indicated SO_2 removal, %	88	81	91	78	89	91	89	85
Slurry from first-stage scrubber[i]								
pH at end of period	5.6	4.3	4.6	4.7	4.1	3.8	3.9	4.2
Composition,[j] % by wt.								
CaO	33	32	40	26	26	39	32	34
Total S	16.1	0.2	2.6	0.1	14.2	21.5	17.2	7.0
Sulfite S	11.2	-	1.3	0.04	0.1	4.8	0.5	4.5
Indicated oxidation,[k] %	30	-	50	-	99	78	97	36
Indicated CaO utilization, %	85	(38)[l]	11	-	97	96	95	36

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[a] Two spray scrubbers 4 inches in diameter by 2 feet long in series, recycling 1% limestone slurry at 9 l./min. to each; about 5 c.f.m. stack gas produced by burning a mixture of natural gas and fuel oil to which carbon disulfide was added.

[b] Spring Valley limestone from Ralph Rogers and Company, Inc., Tuscumbia, Alabama; 76% -200 mesh.

[c] Amount used was 10% of the stoichiometric amount for reaction with the feed limestone unless noted otherwise.

[d] 50% of stoichiometric to react with feed limestone.

[e] Supernatant liquor separated from test 64 was used to slurry the limestone.

[f] Tests were continued for about 5 hr. at steady state.

[g] 1% limestone content.

[h] Values averaged over steady-state period.

[i] Composite over steady-state period.

[j] Solids separated by filtration.

[k] Overall oxidation (both scrubbers).

[l] **Estimated by similarity to other tests.**

Stability of Acids: Two series of tests were made to determine the stability of the four acids under conditions considered to be more drastic than those likely to be encountered in scrubbing operations. These accelerated tests were made with both solutions and melts[1] of the acids as follows:

	Solutions				Melts		
Conditions	Benzoic	Phthalic	Adipic	Glycolic	Benzoic	Phthalic	Adipic
Acid concentration, %	0.3	0.1	2	70	100	112.2[a]	100
Temperature, °C	75	75	75	55	136	212	162
Time, hr	51	53	59	28	18	0.5	10
Composition of gas, %							
SO_2	50	67	50	67	67	67	67
O_2	25	33	50	33	33	33	33
N_2	25	0	0	0	0	0	0
Gas flow rate, ml/min	200	120	40	45	45	45	45

[a] Phthalic anhydride was used rather than phthalic acid.

The ultraviolet absorption of the solutions and melts after treatment was determined as a means of detecting any decomposition of the acids. The solutions after treatment had a strong odor of SO_2. Since the SO_2 interfered with the absorbance measurements, it was eliminated by boiling the solutions for about 10 minutes. Results of the measurements, shown in Figure 1 for benzoic acid,[2] indicate that there was no chemical attack on the acids. There were no new absorption peaks observed in the treated samples as there should have been if decomposition products were present. There was a possibility that some glycolic acid was volatilized from the 70% solution, but this could have been due to our inability to attain the same concentration of the acid, before and after SO_2 treatment, for the ultraviolet absorbance comparison. It was concluded that all four acids were relatively stable.

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[1] Glycolic acid was available only as a 70% aqueous solution; therefore it was not included in the melt tests.

[2] Only the curves for the melt and for benzoic acid volatilized from the melt are shown. Similar results, however, were obtained for the solutions.

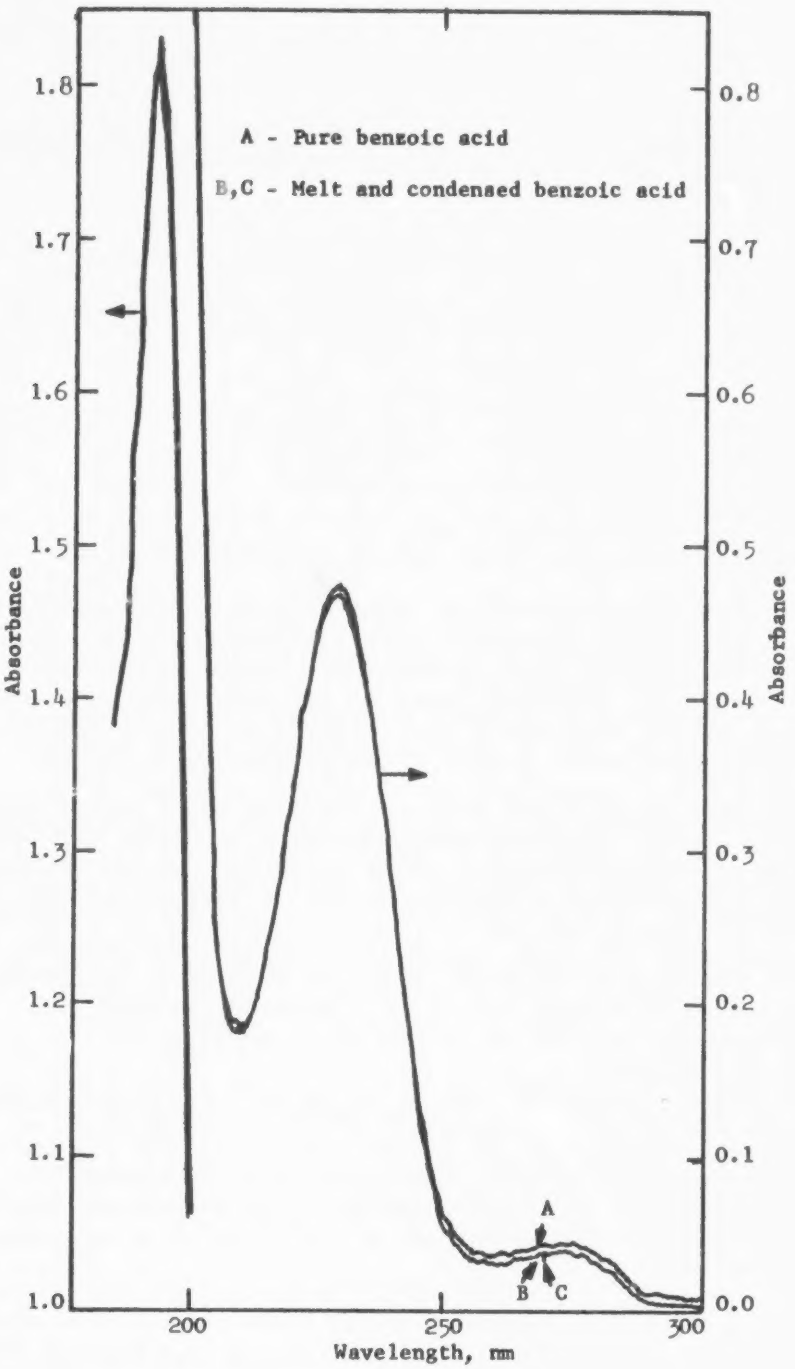

FIGURE 1

Ultraviolet Absorption of Benzoic Acid

Solubility of Salts and Solubilizing Power of Acids: The calcium salts[1] of the four acids were solubilized in water at 25° and 50°C with the following results:

Solubility and pH of Calcium Salts of Organic Acids at 25° and 50°C

Acid	Solubility, % salt by wt.[a]		pH of saturated solution	
	25°C	50°C	25°C	50°C
Benzoic	2.80 (4000)	3.83 (5450)	7.38	6.83
Glycolic	1.52 (3200)	3.24 (6850)	7.08	6.60
Phthalic	0.33 (650)	0.25 (500)	6.36	7.41
Adipic	3.14 (6850)	1.98 (4300)	7.57	7.55

[a] Values in parentheses are ppm Ca in saturated solution.

The solubility of the calcium salts of the monobasic acids (benzoic and glycolic) increased and the pH decreased with temperature. The salts of the dibasic acids (phthalic and adipic) decreased in solubility with temperature. Benzoic, glycolic, and adipic acids are especially promising at 50°C, but phthalic acid gives only about 1/10 of the calcium concentration as compared with the other three acids.

The solubilizing power of the four acids toward $CaCO_3$ and $MgCO_3$ was determined at three concentrations of acid (0.05, 0.1, and 0.2%) at 25°C and at one concentration (0.1%) at 50°C. The results are given in Table V. In each case approximately two carboxy groups were required to dissolve an atom of calcium from $CaCO_3$, regardless of temperature or concentration of acid; for $MgCO_3$, somewhat less than two carboxy groups were required. The pH's of solutions saturated with $CaCO_3$ were about 8 at 25°C and about 7 at 50°C; for the solutions saturated with $MgCO_3$ the corresponding pH values were 9 and 8.3 at 25° and 50°C, respectively.

Effect of Organic Acids on the Rate of Oxidation of Sulfite to Sulfate: The rate of oxidation of sulfite in solution to sulfate by pure oxygen was determined in the presence of the various organic acids. The tests were made at pH = 4 by adding sufficient powdered $CaCO_3$ to maintain the pH constant as oxidation proceeded. The comparison is made in Figure 2 for initial sulfite concentration of 0.0123 molal at an oxygen flow rate of 20 ml/min.

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[1] The magnesium salts were not tested because they could not be prepared in sufficient purity for testing.

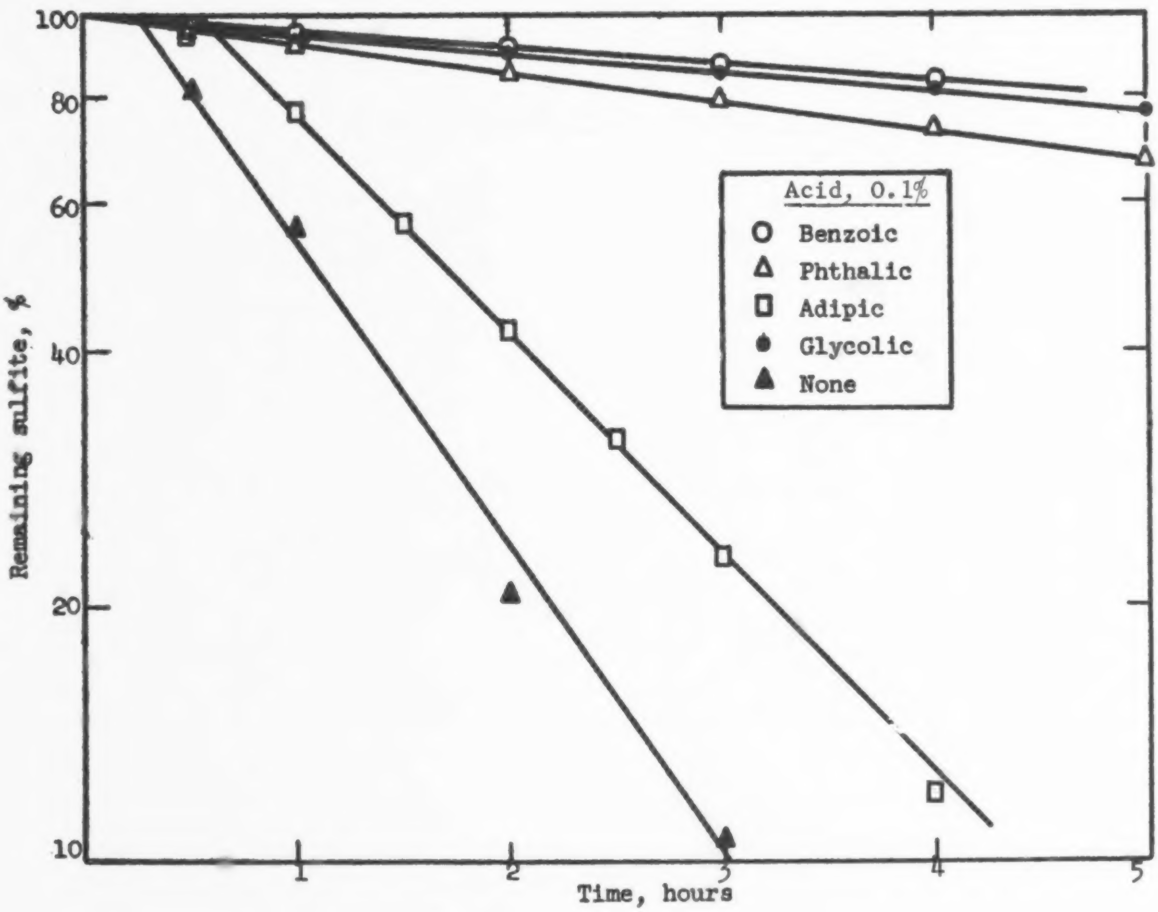

FIGURE 2

Effect of Organic Acids on the Oxidation of Sulfite to Sulfate in Calcium System at 50°C and pH 4.0

TABLE V

Solubilization of $CaCO_3$ and $MgCO_3$ by Organic Acids

Effect of Concentration of Acid at 25°C

Acid	ppm Ca when acid concn., %, is			ppm Mg when acid concn., %, is		
	0.05	0.1	0.2	0.05	0.1	0.2
Benzoic	97	180	340	140	210	330
Glycolic	130	270	550	170	280	460
Phthalic	130	240	480	160	250	420
Adipic	150	290	570	170	280	470

Effect of Temperature When Acid Concentration is 0.1%

Acid	pH		ppm Ca		pH		ppm Mg	
	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
Benzoic	7.95	7.18	180	180	9.1	8.5	210	200
Glycolic	7.98	6.69	270	350	9.1	8.2	280	300
Phthalic	8.00	6.77	240	250	9.2	8.4	250	260
Adipic	7.92	6.80	290	320	9.1	8.3	280	290

Benzoic, glycolic, and adipic acids, at 0.1% in solution, retarded the oxidation of sulfite; less than 40% of the original sulfite was oxidized in 5 hours when these acids were present, whereas 42% of the sulfite was oxidized in 1 hour when no additive was present. Adipic acid has some retarding effect on oxidation, but not as great as the other three acids. The curves for adipic acid and no additive do not plot into 100% at zero time, indicating an initial quiescent period before the oxidation proceeds. The first order rate constants for oxidation as determined by the curves in Figure 2 are:

Acid	$K \times 10^6$, sec^{-1}
None	43.0
Benzoic	2.4
Glycolic	2.9
Phathalic	4.3
Adipic	32.0

A similar comparison of benzoic acid with no additive was made at an initial pH of 4.0 but without holding the pH constant during the oxidation.

Three replicas of the test without additive were made to determine the reproducibility of the oxidation rates and also because of the difficulty in obtaining identical starting solutions. The results are shown in Figure 3.

When benzoic acid was present at 0.16% the pH changed much less rapidly as oxidation proceeded than when it was absent. Again, the amount oxidized in 1 hour with no additive was greater than that oxidized in 5 hours with benzoic acid present--indicating a retardation effect of the rate of oxidation by benzoic acid.

These results do not appear compatible with those obtained in exploratory tests on SO_2 absorption (Table IV), in which the sulfate:sulfite ratio in the product solids was higher when organic acids were used. This may have been due to the fact that excess sulfite crystals were present in the absorption tests. At the lower pH resulting from the acid addition (on the order of 1.5), this would produce a much higher dissolved sulfite concentration in the solutions containing organic acid, and therefore might promote the transition $CaSO_3 \cdot 0.5H_2O_{(c)} \rightarrow CaSO_3 \cdot 0.5H_2O_{(l)} \rightarrow CaSO_4 \cdot 2H_2O_{(l)} \rightarrow CaSO_4 \cdot 2H_2O_{(s)}$ even if the oxidation rate in the solution phase were reduced by presence of the acid.

Aqueous Species: The thermodynamic dissociation constants of the acids[1,2] at 25°C are as follows:

Acid	log K_1	log K_2
Benzoic	-4.205	-
Glycolic	-3.831	-
Phthalic	-3.14	-5.40
Adipic	-4.42	-5.41

These constants denote the pH at which the activities of the undissociated acid and the organic anion are equal; for example, the activity of benzoic acid, HBz, equals the activity of the benzoate ion, Bz^-, at pH 4.2, etc.

Analysis of the solubility and pH data of Table V indicate that the benzoate ion forms a weak complex, $CaBz^+$, for which the following equilibrium constant is obtained:

$$CaBz^+ \rightleftarrows Ca^{++} + Bz^- \quad K^* = 10^{-2.13 \pm 0.15} \text{ at } 25°C$$

$$K^* = 10^{-1.0 \pm 0.5} \text{ at } 50°C$$

This compares with the only reported literature value of $\sim 10^{-0.2}$ by Bunting and Thong[3] at 30°C and an ionic strength of 0.4; this latter value becomes $10^{-0.8}$ at $I = 0$, using the Davies activity coefficients.

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[1] Stability Constants, Special Publication No. 17, The Chemical Society (1964).
[2] Smolyakov and Primanchuk, Russ. J. Phys. Chem. 40 (3), 331-3 (1966).
[3] Can. J. Chem. 48, 1654-6 (1969).

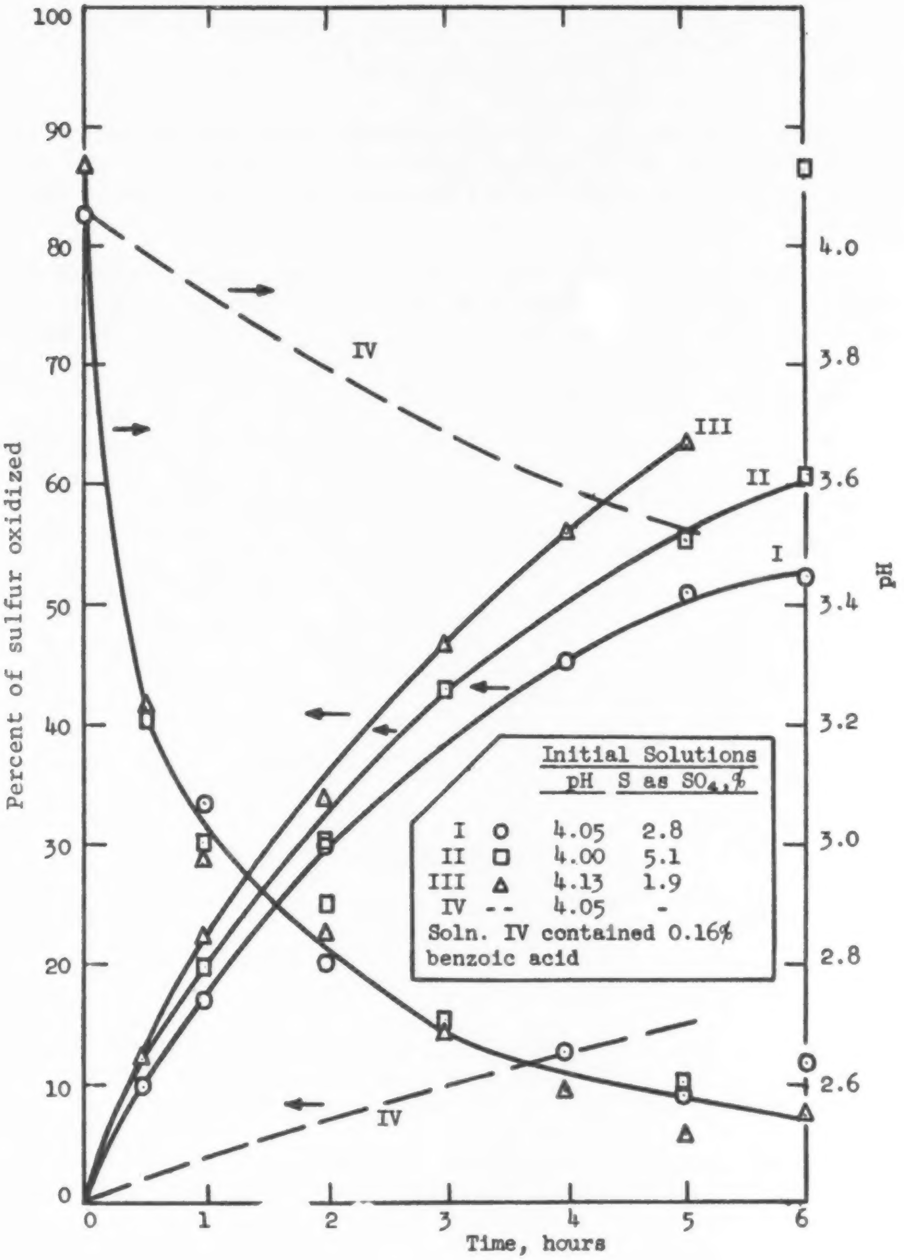

FIGURE 3

Oxidation of Sulfite to Sulfate in the System $CaO-SO_2-SO_3-H_2O$ at 50°C With O_2 Gas

The calculation of stability constants from solubility data requires very accurate data both with respect to the component concentrations and the pH of the solution. Benzoic acid has very sharp ultraviolet absorption peaks, and its chemical determination is much more precise than that of glycolic, phthalic, or adipic acids. Even so, the dissociation constant calculated from the data in Table V was not confirmed by the solubility of the salt, $CaBz_2$--again due to the sensitivity of the data. No consistent values of dissociation constants for complexes of Ca or Mg with glycolic, phthalic, or adipic acids were obtained from either the dissolution of carbonates (Table V) or the solubility of the salts; in many cases the data gave negative values for some of the assumed species.

The significance of the value of the dissociation constant of the complex $CaBz^+$, K^*, is shown in the following tabulation of the amount of calcium required to complex various amounts of the benzoic acid for two values of K^* when the benzoic acid concentration is approximately 0.1%:

Degree of complexing as $CaBx^+$, %	ppm Ca required if $K^* = 10^{-2.13}$	ppm Ca required if $K^* = 10^{-1.0}$
10	30	300
50	300	3,000
90	3,000	30,000

A further attempt to determine the presence of an aqueous complex was made using both ultraviolet absorption and calcium ion specific electrode with Job's method of continuous variation of the ratio Bz:Ca in solution. The ultraviolet absorption data showed a strictly linear increase in absorbance with total benzoate concentration with no breaks or irregularities due to a significant amount of $CaBz^+$ species. The specific ion electrode measurements were not definitive but did indicate a small amount of calcium that was other than ionic Ca^{++}; this could have been $CaOH^+$, $CaHCO_3^+$, or other known species in addition to $CaBz^+$. The conclusion is that if a complex between calcium and benzoic acid is formed, it is a weak complex (highly ionized) that defies accurate measurements by the methods attempted.

Small-Scale Tests with Benzoic Acid

Continuous scrubbing tests with benzoic acid were made in the 5-cfm two-stage scrubber described earlier except that commercial spray nozzles were used which permitted operation at a liquid rate of 700 ml/min (37 gal/Mcf) in each tower. Limestone slurry (with filtrate recycled) was added to the second tower to scrub the gas, and water was added to the first tower to humidify and cool the gas before scrubbing. The flue gas was obtained by burning natural gas, with SO_2 added from a cylinder to obtain about 3000 ppm in the gas. This procedure simulated closed-loop operation under conditions of about 50% SO_2 removal so that the effects of an organic acid added to the limestone slurry could be tested. The results are shown in Table VI.

TABLE VI

Effect of Benzoic Acid on Sulfur Dioxide Absorption by Limestone Slurry[a]

	Test No. 1	Test No. 2	Test No. 3
Recycle slurry			
Benzoic acid added, %[b]	0	50	75
pH at end of period	4.5	3.7	4.3
Stack gas			
Inlet temperature, °F	205	210	210
SO_2 content, ppm			
To first-stage scrubber	3150	3150	3125
From second-stage scrubber	1565	915	740
Indicated SO_2 removal, %	50	71	76

---

[a] First scrubber of water recycling at about 700 ml/min; second of limestone slurry recycling at 700 ml/min.

[b] Percent of that required to solubilize lime for reaction with all the SO_2 entering the system.

Adding benzoic acid to the slurry in an amount equivalent to that required to solubilize 50% of the lime required for reacting with the SO_2 feed increased the SO_2 removal from 50 to 71%; 75% of stoichiometric gave a further increase to 76% SO_2 removal. Other runs (not shown) with lesser fractions of benzoic acid were made with intermediate results. The results of the improvement in SO_2 removal with the percent of stoichiometric benzoic acid for lime solubilization are shown in Figure 4. The results indicate a rather steep increase in SO_2 removal for the first 25% of stoichiometric acid and a leveling of the response beyond this amount.

An extended closed-loop test was made using 20% of the stoichiometric amount of benzoic acid. No apparent loss in the efficiency of the slurry to remove SO_2 was noticed in 18 hours, indicating that the losses of benzoic acid were probably low. A similar test using 150% of the stoichiometric benzoic acid indicated, by ultraviolet absorption analysis of the liquid, about 1% loss per hour.

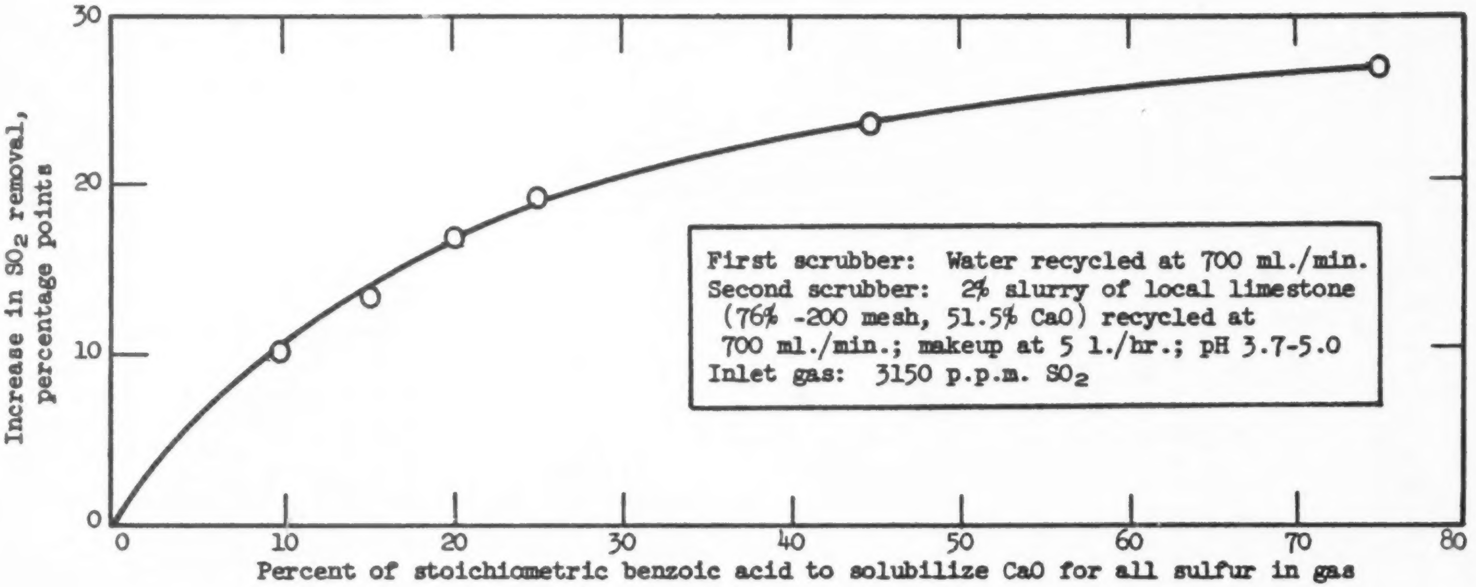

FIGURE 4

Effect of Proportion of Benzoic Acid

Added to Limestone Slurry on Sulfur Dioxide Removal

The vapor pressure of benzoic acid at 0.16% was determined between 40° and 65°C (104° and 149°F) and was expressed by least squares by

$$\log P_{HBz} = 9.20 - 4787/T$$

where T is the absolute temperature, °K. This implies an energy of evaporation of benzoic acid of 22 kcal/mole from solution, compared with 21.9 kcal/mole for sublimation of the pure acid. The dependence of Henry's law constant, h, for benzoic acid absorption becomes

$$\log h = -10.27 + 4500/T$$

and the vapor pressure of 0.01 molar benzoic acid at various temperatures and pH's are as follows:

	Vapor pressure, ppb when temperature is		
pH	45°C (113°F)	50°C (122°F)	55°C (131°F)
2	136	217	355
3	129	206	337
4	85	137	225
5	19	31	52
6	2	4	6

These values indicate that losses from evaporation will be relatively low in the range of scrubber conditions. However, a vapor pressure of 100 ppb of benzoic acid would result in the loss of about 2.5 lb of benzoic acid per hour if used to scrub the gas from a 500-mw boiler. It is likely that other losses, through adsorption on solids and faulty mist eliminators, will be more important than evaporation *per se*.

Summary

The use of certain weak organic acids, particularly benzoic, appears promising as a means of improving the effectiveness of limestone slurry in removing SO_2 from stack gas. It has been determined that the stability, volatility, and calcium salt solubility for benzoic, adipic, phthalic, and glycolic acids are within ranges that appear acceptable for practical operation. Only small amounts, on the order of 20 to 40% of that needed to dissolve the stoichiometric quantity of limestone (based on amount of SO_2 to be removed), are required to effect a major increase in SO_2 absorption efficiency.

The method has the further promise of increasing limestone utilization. If all the feed limestone were dissolved in the organic acid, the limestone should remain in the scrubber loop until completely reacted; without the organic acid, part of the limestone is lost with the waste solids because complete conversion of $CaCO_3$ to $CaSO_3 \cdot 0.5H_2O$ is never obtained in one pass through the scrubber.

The potential advantages of organic acid addition are such that further work is planned, both on a small scale and in pilot plant tests.

POTENTIAL WATER QUALITY PROBLEMS ASSOCIATED WITH LIMESTONE WET SCRUBBING FOR SO_2 REMOVAL FROM STACK GAS

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The present emphasis on rapid attainment of a higher quality total environment has focused added attention on the interrelated effects on air, water, and land resources that result from new technology for controlling pollution. An inescapable byproduct of any separation process is a concentrated waste. Without waste recovery it is rarely possible to develop practical control methods for specific wastes in any one of these three natural resource areas without affecting at least one of the other two areas. In the limestone scrubbing process for control of sulfur dioxide, land use is affected by the necessity for disposing of large quantities of solid waste material, and discharge of once-through scrubber water or bleed-off from recirculating systems to receiving streams presents a potential problem of water quality degradation.

A scrubber system based on a lime process has a somewhat different effect on water quality than one based on limestone. In evaluating the potential for each process, TVA has concluded that the use of lime appears infeasible because the system requires (1) dilution of the scrubber liquor, which necessitates an "open loop" operation with an overflow to a watercourse, or (2) use of a very expensive, high rate of recirculation. Since most of TVA's efforts have thus been confined to limestone scrubbing, the following discussion is of this basic process.

Potential Pollution Problems

Table 1 lists the soluble cation constituents of the effluent from a typical limestone scrubber. This semiquantitative spectrographic analysis indicates the wide range of cationic species found in such a system. These constituents, together with the associated anions--mostly SO_3, SO_4, and NO_3--and the pH and suspended solids, represent the potential water pollutants. It is assumed that operation of a scrubber system will provide adequate settling for solids; thus, suspended material will not adversely affect water quality.

The minor and trace elements shown in table 1 require quantitative analysis because of the low concentrations permissible under existing standards. The maximum stream concentrations of the following elements are based on allowable limits for potable water: manganese, 0.05 mg/l; zinc, 5.0 mg/l; silver, 0.05 mg/l; copper, 1.0 mg/l; and lead, 0.05 mg/l. Stream standards generally apply to the concentrations existing after the effluent is fully mixed with the receiving waters.

Adverse effects from various concentrations of the remaining trace cations are included in the Water Quality Criteria publication of the Resources Agency of California referred to in the appendix. With the exception of zinc, manganese, and copper, TVA has not quantitatively analyzed the minor and trace elements listed. Chemical analysis of scrubber water during one preliminary pilot-plant run resulted in the following maximum concentrations: manganese, 80 mg/l; zinc, 9.0 mg/l; and copper, 5.0 mg/l. Each of these concentrations would likely exceed limits for an effluent standard, and manganese would likely exceed applicable stream standards.

TABLE 1

SPECTROGRAPHIC ANALYSIS

Element	Relative Distribution
Calcium	Major
Iron	Major
Aluminum	Major
Silicon	Major
Magnesium	Major (-)*
Sodium	Major (-)*
Potassium	Major (-)*
Titanium	Major (-)*
Manganese	Minor
Zinc	Minor
Tin	Trace
Copper	Trace
Silver	Trace
Vanadium	Trace
Molybdenum	Trace
Galium	Trace
Mercury	Trace**
Lead	Trace**
Boron	Trace
Nickel	Trace

*Less than other major components, but more than minor quantities.

**Quantity is at the lower limit of detection for emission spectrograph.

Quantitative analysis of the major soluble constituents from flyash and limestone together with some preliminary data from pilot-plant operation indicate that the characteristics of the scrubber water that are of most concern, relative to potential for adverse effects on water quality, are those shown in table 2. Table 2 also indicates an approximate allowable concentration of each constituent based on various regulatory standards and on criteria recommended by TVA. Although limits generally apply to the concentrations after mixing, strict adherence to a nondegradation standard or adoption of an effluent standard might require that these limits not be exceeded in the discharge itself. Effluent standards, such as those recently adopted by the Ohio River Sanitation Commission for the Ohio River, are becoming more prevalent with increased demand for more stringent controls.

A general discussion of the detrimental effects of the more important of these characteristics is presented in the appendix.

TABLE 2

MAXIMUM ALLOWABLE CONCENTRATIONS

		*Maximum Concentration Milligrams per Liter
Calcium Magnesium	Hardness (as $CaCO_3$)	200
Sulfate		150
Chloride		150
Total Dissolved Solids		500
pH		6.5 - 8.5

*Based on various regulatory standards and TVA criteria for receiving streams.

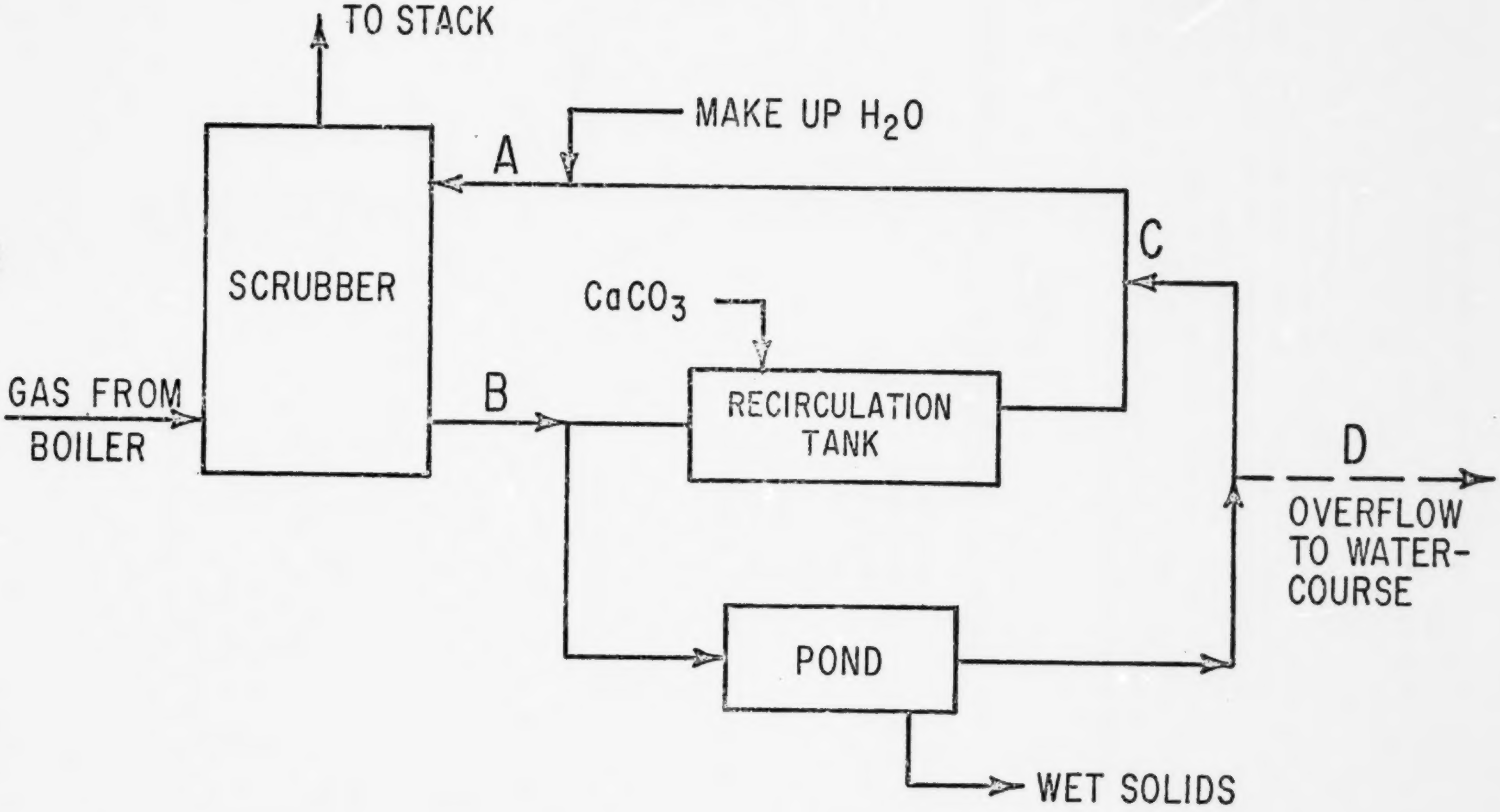
Concentration of Pollutants

The constituents listed in tables 1 and 2 are likely to be present in any scrubber solution; however, if one disregards the threat to the aqueous environment from system leaks and pond seepage, the real potential for degradation of water quality is due to any scrubber solution discharged to the receiving waters. Since operation of a scrubber system with complete recycle increases the problems of scaling and may cause operational problems due to the buildup of dissolved salts, many systems are being designed to discharge some of the scrubber water. Figure 1 shows a simplified diagram of a typical limestone scrubbing system. Item D, the discharge from the settling pond, may be any portion of the total contents of the pond from no discharge to 100 percent discharge. No discharge would represent a fully closed-loop system with no potential for pollution, and this system is discussed only in the conclusion. The following discussion is confined to partial bleed-offs and to 100 percent discharge.

Table 3 shows the theoretical concentrations in scrubber water from a limestone process utilizing a 3 percent MgO limestone, a 150 percent stoichiometric limestone feed for 3.5 percent sulfur coal, 100 percent NO_2 absorption, 100 percent MgO reaction, 25 percent formation of calcium sulfate, and 75 percent formation of calcium sulfite. This theoretical analysis is based on the simultaneous solution of assumed solubility equations. The analysis represents the buildup of concentrations for a system with 100 percent recycle; a system with a partial bleed-off, with the necessary makeup of fresh water, would be expected to contain somewhat lower concentrations. The reduction in concentrations is dependent on the percentage of scrubber water discharged; however, for bleed-offs

FIGURE I

TYPICAL SCRUBBER FLOW SYSTEM



of 20 to 30 percent, the reduction is not expected to be significant from the standpoint of water quality. Table 4 compares the theoretical concentrations with preliminary data from a pilot plant with a similar operating system. The pilot-plant feed was approximately 100 percent stoichiometric, and the MgO content was about 1 percent. The major differences between these calculated and measured concentrations are in the concentrations of sulfites and nitrates. The theoretical assumptions regarding NO_2 absorption are apparently erroneous, since no pilot-plant data reviewed to date indicate more than 10 mg/l NO_3. The higher sulfite concentration in the results for the pilot plant may indicate a formation of $MgSO_3$, although no satisfactory balance of the complexes can be made from the data. The most important information from the pilot-plant data is not obtained from an analysis of the differences between them and the calculated values, but from the conclusion that the high concentrations of potential pollutants theoretically predicted may actually occur in the system.

TABLE 3

THEORETICAL CONCENTRATIONS IN SCRUBBER POND EFFLUENT

Calcium	950 mg/l
Magnesium	3,500 mg/l
Hardness (as $CaCO_3$)	16,500 mg/l
Sulfite	150 mg/l
Sulfate	9,500 mg/l
Nitrate	7,750 mg/l
Sodium	850 mg/l
Total Dissolved Solids	25,000 mg/l
pH	6.0

TABLE 4

COMPARISON OF THEORETICAL CONCENTRATIONS WITH PRELIMINARY PILOT PLANT DATA

	Theoretical Concentration Milligrams per Liter	Pilot Plant Concentration Milligrams per Liter
Calcium	950	1,600
Magnesium	3,500	1,150
Hardness (as $CaCO_3$)	16,500	7,100
Sulfite	150	5,400
Sulfate	9,500	6,500
Nitrate	7,750	1
Sodium	850	26
Total Dissolved Solids	25,000	13,000
pH	6.0	5.0

The high quantities of dissolved salts in these scrubber systems represent a significant potential for creating a problem of water pollution. Utilization of other limestones in different modes of operation may create greater or lesser potential problems; however, for partially closed-loop operations, table 4 should generally be representative. In situations where stringent effluent standards are implemented or where strict interpretation of a nondegradation standard is enforced, it is doubtful if scrubber waters can be discharged without a very high degree of treatment. The potential adverse effects from such discharges--regardless of standards--are dependent on the quantity of bleed-off and the flow of the receiving stream.

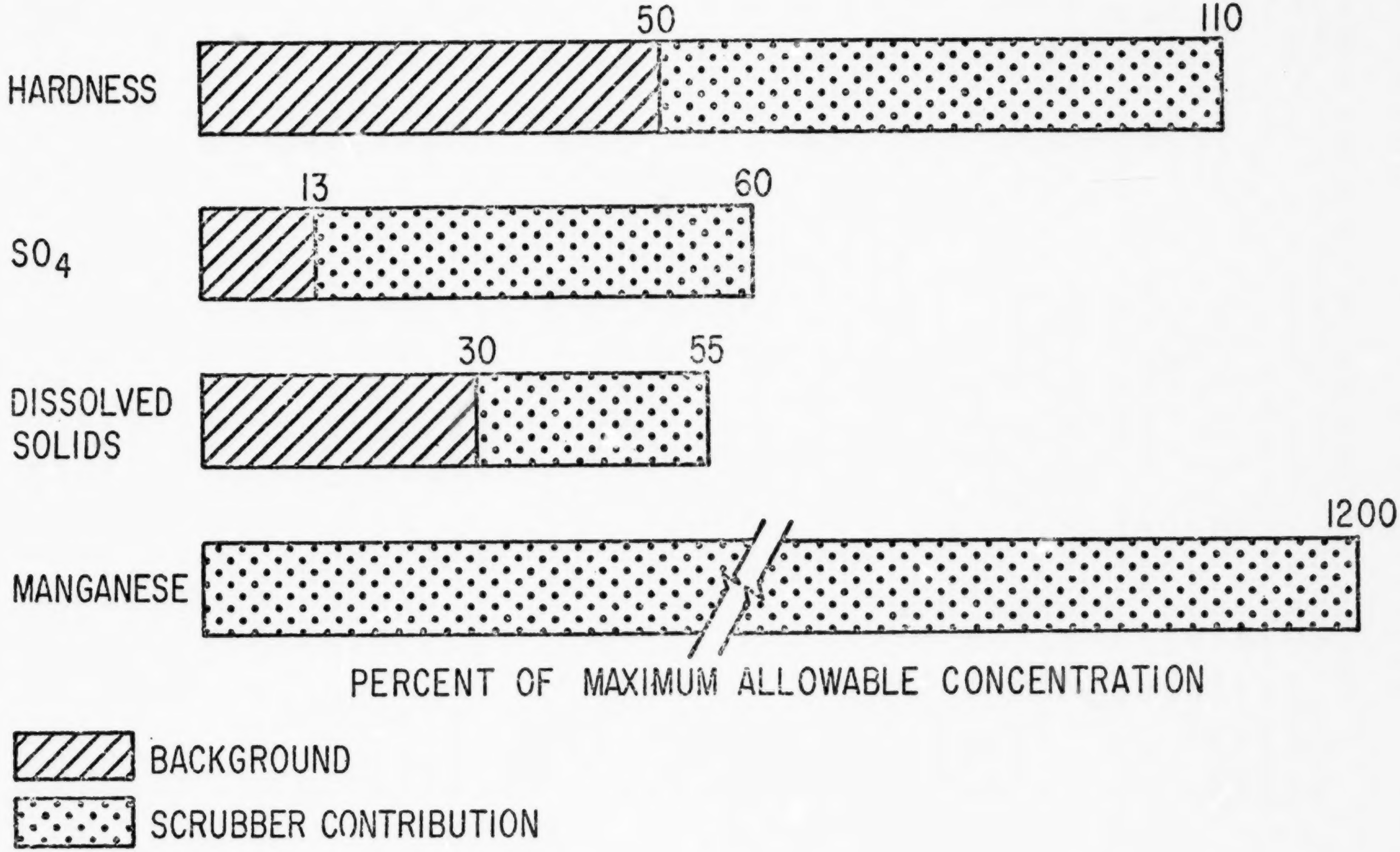
The effects on a receiving stream from the release of such concentrations were calculated for a hypothetical 1500-megawatt plant with an assumed bleed-off of 30 percent, equivalent to about 4,500 gpm, and an assumed dilution ratio of the receiving stream to plant discharge at critical low stream flow (7 day-10 year minimum) of 135 to 1. The ratio is obtained by assuming that the critical low flow is equivalent to the condenser cooling water required for plant operation, 600,000 gpm or 1340 cubic feet per second. Although this may seem extreme, a random survey of some 20 existing plants indicated that two plants are located on streams that have much less relative stream flow. It is not actually necessary to assume any plant size, since the ratio of discharge to available dilution would remain the same in all cases; however, the assumptions indicate that the critical flow levels are representative of fairly large rivers. Figure 2 shows the resulting percentage of total allowable concentration assuming typical background concentrations of 100 mg/l hardness as $CaCO_3$, 20 mg/l SO_4, 150 mg/l total dissolved solids, and 0 mg/l manganese, complete mixing in the stream, and a scrubber discharge containing the theoretical concentrations shown in table 4 less the nitrate concentrations. The manganese concentration was taken from the pilot-plant data. Although only hardness and manganese exceed the assumed limits, the percentage increase in the concentration is quite significant. Such increases in total stream concentration are not generally acceptable. Refer to the appendix for a discussion of actual adverse effects from the resulting concentrations.

One potential water-quality problem, that of the dissolved sulfite concentration, appears to be much less severe than originally anticipated and may, in fact, be quite insignificant. High concentrations of sulfite will utilize large quantities of dissolved oxygen in the oxidation to sulfate: 0.2 milligrams of oxygen per milligram of sulfite. The presence of certain metals in the flyash, such as iron, was thought to be sufficient catalyst for the oxidation of sulfite to proceed rapidly enough to significantly lower the dissolved oxygen in the settling pond and ultimately in the receiving stream. From pilot-plant results, it now appears that this reaction proceeds quite slowly and, indeed, may be difficult to induce.

A complete theoretical computation of the chemical characteristics of the effluent from the settling pond for a limestone scrubbing system operating with a 100-percent overflow has not been made; however, some pilot-plant data have been analyzed. Table 5 compares pilot-plant data obtained during open-loop operation with those obtained during closed-loop operation. The open loop operated with 1 percent MgO limestone and a limestone feed of approximately 150 percent stoichiometric for a unit burning coal with 3 percent sulfur. Although the concentrations are less for the open loop, they are surprisingly high and of

FIGURE 2

STREAM CONCENTRATIONS AT LOW FLOW



such magnitude as to be of concern. If the concentrations for closed-loop operation are assumed to be representative of a 30-percent bleed-off, then the total quantities of waste constituents discharged from each of the operational modes are similar. The greater flow of the open-loop process (more than three times that of the closed-loop system) produces somewhat greater amounts and, therefore, a greater potential for adverse effects on water quality.

TABLE 5

CONCENTRATIONS IN OPEN-AND CLOSED-SCRUBBER SYSTEMS

	Closed-Loop Mode Milligrams per Liter	Open-Loop Mode Milligrams per Liter
Calcium	1,600	1,100
Magnesium	1,150	*
Hardness (as $CaCO_3$)	7,100	**2,700
Sulfite	5,400	1,700
Sulfate	6,500	2,600
Nitrate	1	6
Total Dissolved Solids	13,000	**7,000
pH	5.0	5.3

*Not determined, MgO content of limestone less than 1%.

**Not determined, estimated minimum values.

Factors That Affect the Quality of Scrubber Water

Almost all input factors in a limestone scrubbing system will affect the quality of scrubber water and its potential for water pollution. In particular, the coal, limestone, feed rate, type of boiler, type of scrubber, ratio of liquid to gas, and pH of the scrubber water will have major effects on the characteristics of the scrubber water.

The oxidation of sulfites to sulfates in the system will have a major bearing on the quantity of dissolved salts in the system and, according to TVA pilot plant results, will greatly affect the settling characteristics of the reaction products. If the solids are mainly calcium sulfite rather than calcium sulfate, as has been the case in much of TVA's work on the closed-loop system, settling is very poor. The thin sulfite platelets form a gel-like structure that settles very slowly. Although this settling problem has no direct effect on water quality, the settling pond for the gel-like substance would certainly require careful design to assure containment adequate to prevent any threat to nearby watercourses. While formation of sulfate may be more desirable from the standpoint of settling, it may create a greater potential for direct water pollution. The sulfate reaction products are much more soluble than the sulfites, more than 50 times as soluble in the case of the calcium products; thus, higher concentrations of dissolved salts result from increased oxidation.

The chemical makeup of the limestone is quite important in defining the potential effects on water quality. Among the major controlling characteristics of the limestone is its magnesium content, which has an important bearing on waste disposal because of the high solubility of magnesium sulfate. There is some indication that small amounts of magnesium may appear as magnesium hydroxide rather than sulfate in the products; this is desirable because the hydroxide is extremely insoluble. In many areas of the country, however, calcitic limestones are not readily available, and dolomite ($CaCO_3 \cdot MgCO_3$) or dolomitic limestone would be the raw material. Figure 3 shows the concentration of sulfates and hardness of the scrubber water as functions of the MgO content of the limestone.

Conclusion

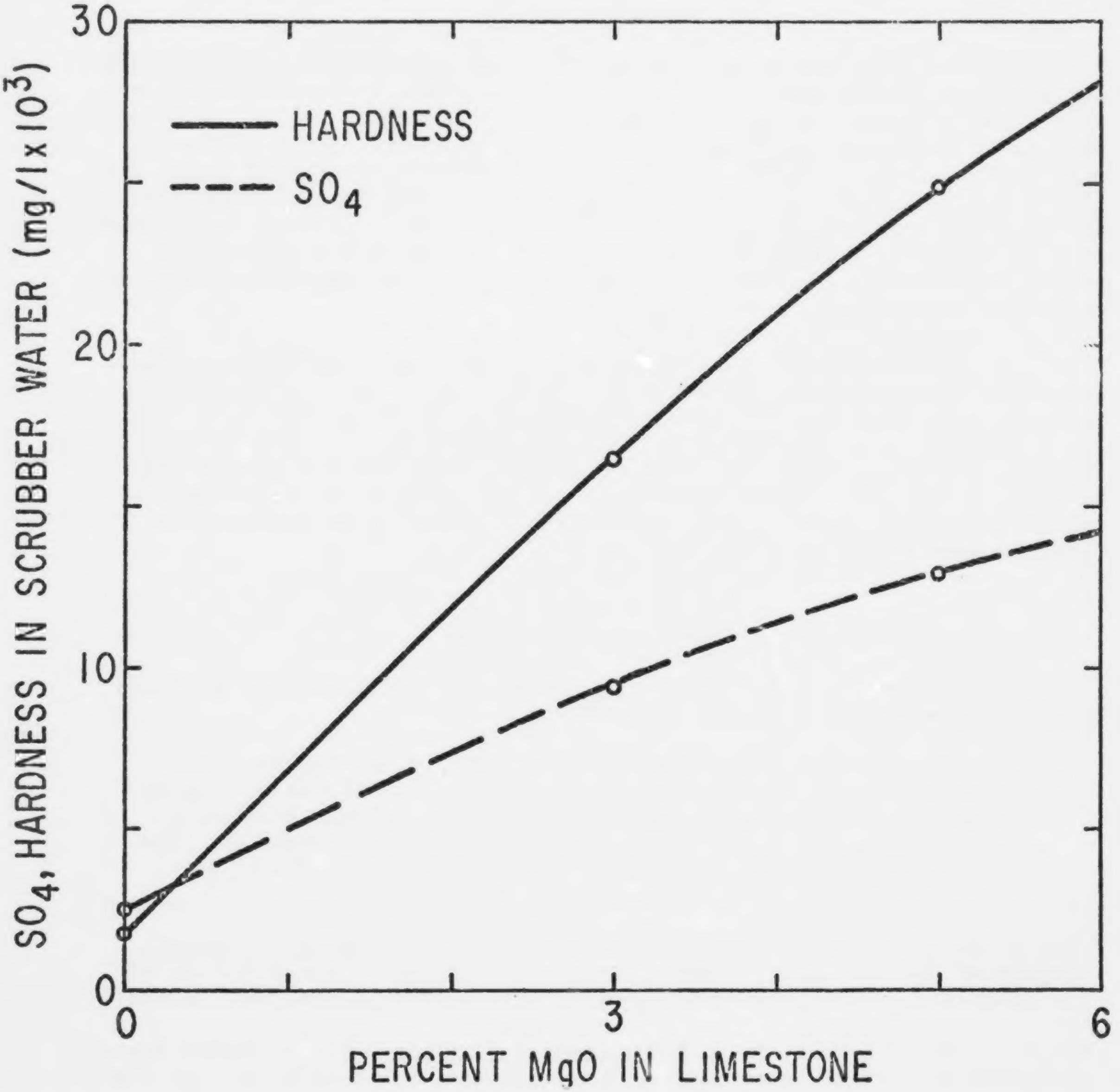
A given concentration of a pollutant has the same detrimental effect on water quality no matter what its source, but a minor detrimental effect from the residual waste discharge from an efficient production process and treatment facility might be considered acceptable while the same effect, if it results from an attempt to provide control of wastes from other sources sufficient to meet an applicable standard, might not be considered acceptable. TVA believes that a solution to a problem of air pollution that in turn creates a problem of water pollution--even though possibly one of lesser extent--is not satisfactory. Thus, TVA's full-size experimental unit being designed for installation on unit 8 of the Widows Creek Steam Plant will be a closed-loop operation with no degrading of water quality.

If an open loop is absolutely necessary for other systems, their continued operation, in the immediate future, will be dependent on the characteristics of the waste from the process, the quantity of discharge, and the size of the receiving stream. It seems increasingly evident, however, that more stringent controls, the implementation of effluent standards, and strict enforcement of nondegradation policies will require a closed cycle or a high degree of treatment. Although no thorough investigation of technically feasible methods of treatment has been made, wastewater containing such high concentrations of dissolved solids as are present in the scrubber flow generally requires advanced, sophisticated, and often expensive treatment. Treatment by distillation is considered technically feasible, but since the estimated annual capital and operating cost for treating a 30-percent bleed-off from a 1500-megawatt plant is $1.5 to $2.0 million, this method is economically infeasible. Although other treatment methods may be technically adequate and more economical, most processes still require disposing of a concentrated waste product. Based on the present state of the art of treatment of such wastes and environmental considerations, complete recycle of the scrubber water, wherever technically feasible, should be the operational mode for limestone systems.

Although it is quite apparent that limestone scrubbing systems can have a potential for affecting water quality, the magnitude of this potential is not adequately defined. TVA is continuing its efforts to gain additional information. The Radian Corporation recently began a complete chemical analysis of TVA's pilot-plant scrubbing process, and the resulting data will be used to refine the theoretical analysis of the system and to aid in evaluating effects on water quality. The large-scale lime/limestone scrubbing tests scheduled to begin in March 1972 at the TVA Shawnee Steam Plant will provide an opportunity to further define the effects of various scrubbers and operating parameters.

FIGURE 3

EFFECT OF MgO CONTENT OF LIMESTONE ON HARDNESS AND SO_4 OF SCRUBBER POND EFFLUENT



APPENDIX

The feasibility of releasing dissolved or suspended calcium salts into watercourses depends on how much the content of these impurities in the watercourse is increased, which in turn depends on the amount of the particular pollutant released in the effluent, the content in the watercourse before influx of the effluent, and the water volume flow of the watercourse. Various regulatory agencies and advisory groups have set or recommended limits above which the concentration of an impurity in a watercourse should not be increased. Such limits for the dissolved salts released from a limestone-wet scrubbing process are summarized herein.

Suspended Solids

Most regulatory agencies do not place quantitative limits on either suspended solids or turbidity for raw water used as a source for domestic water, but do generally specify that concentrations shall not be sufficiently high as to be objectionable or interfere with normal treatment processes. Both turbidity and suspended solids can be reduced to acceptable limits for most purposes by conventional treatment methods; however, high concentrations increase the cost of processing the water by increasing chemical requirements and the volume of sludges to be disposed of. In some cases head losses through the filters are increased with a resulting increase in the frequency of filter backwashing.

Settleable suspended solids often blanket stream bottoms, killing fish eggs and young and destroying much of the normal benthic biota which serve as food organisms required for propagation and growth of fish. Turbidity in streams also interferes with light penetration and limits or diminishes the photosynthetic effects necessary for the primary productivity of fish-food organisms. The Committee on Water Quality Criteria of the Federal Water Pollution Control Administration[1] recommends a limit of 50 Jackson Turbidity units in warm water streams.

Total Dissolved Solids

The following information is quoted from Water Quality Criteria, issued by the Resources Agency of California.[2]

> (a) Domestic Water Supplies. The 1962 USPHS Drinking Water Standards specify that the total dissolved solids should not exceed 500 mg/l if more suitable supplies are, or can be made available. This limit was set primarily on the basis of taste thresholds. The 1958 WHO International Standards set the "permissible limit" at

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[1] Federal Water Pollution Control Administration. Water Quality Criteria (Report of the National Technical Advisory Committee to the Secretary of the Interior). U.S. Government Printing Office, Washington, D.C. (April 1, 1968).

[2] McKee, J. E., and Wolf, H. W. Water Quality Criteria. The Resources Agency of California, State Water Quality Control Board, Publication No. 3-A (1963).

500 mg/l and the "excessive limit" at 1500 mg/l, but no "maximum allowable limit" is given. The 1961 WHO European Standards do not include limits for total dissolved solids. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l; however, higher concentrations may be consumed without harmful physiological effects and may indeed even be more beneficial. Each water with a total salt concentration over 1000 mg/l should be judged on the basis of the local situation, alternative supplies, and the reaction of the local population.

(e) Fish and Aquatic Life. It has been reported that among inland waters in the United States supporting a good mixed fish fauna, about 5% have a dissolved-solids concentration under 72 mg/l; about 50% under 169 mg/l; and about 95% under 400 mg/l.

Water quality objectives adopted by TVA for surface water in the Tennessee River basin include a limit of 500 mg/l of dissolved solids.

pH

TVA has proposed upper and lower pH limits for the waters of the Tennessee Valley of 8.5 and 6.5, respectively. The pH values required for industrial water supplies are covered in some detail in the FWPCA Water Quality Criteria report. The proposed TVA criteria should be adequate for all of these but a few extreme cases.

Calcium

Calcium in water supplies has been suspected of producing undesirable physiological reactions but no definite relationship has yet been established. The major concern is related more to its deleterious effects in uses such as washing, bathing, and laundering and to the problem of incrustations on cooking utensils and water heaters. Some industrial processes require a very soft or low calcium water. Costs of conditioning water for such industries is directly related to source concentration.

Thus the major detrimental effect of calcium hardness is economic. TVA has proposed the following limitation on water hardness:

> There shall be no substance added to the waters that will increase the hardness to such an extent as to appreciably impair usefulness as a source of water supply or interfere with other reasonable and necessary uses of the water.

Rivers in the Tennessee Valley on which steam plants are located generally range from 50 to 125 mg/l hardness as calcium carbonate. In general, a concentration of 100 mg/l would not be objectionable for most uses if this concentration were not significantly greater than the normal range for the area.

Calcium Sulfate

No limits have been placed on calcium sulfate by regulatory agencies. The following summary of beneficial uses and reported acceptable concentrations is quoted from McKee and Wolf.

> (a) Domestic Water Supplies. High calcium sulfate concentrations in water are disadvantageous for most household uses, but for drinking purposes, 300 mg/l or more is not harmful. The taste threshold of calcium sulfate has been reported to be 250 to 900 mg/l. Calcium sulfate significantly increases plumbosolvency; raising the calcium sulfate concentration from 25 to 250 mg/l increased by 10 percent the amount of lead dissolved from lead pipes.
>
> (b) In general, calcium sulfate is beneficial in the brewing industry, for it helps to maintain the acidity of the wort and therefore causes more complete coagulation of albuminous matter. It also reduces the solubility of the bitter substances of the hop.
>
> (c) Irrigation. Gypsum in irrigation waters improves or restores the permeability and tilth of soil having an unfavorable sodium ratio.
>
> (d) Stock and Wildlife Watering. A saturated solution of calcium sulfate, used as the sole source of drinking water for rats, permitted satisfactory growth. A concentration of 2400 mg/l of calcium sulfate permitted normal growth and reproduction among rats.
>
> (e) Fish and Other Aquatic Life. Trama reported that a saturated solution of calcium sulfate at 20° C did not produce significant mortalities among bluegills; but a later report from the same organization indicated that this concentration was the 96-hour TL_m at 18-20° C in soft water for the bluegill sunfish. It was also reported that 3200 mg/l caused a 50 percent reduction in the rate of growth of the diatom, *Navicula seminulum*. Using highly turbid water at 21-25° C and the mosquitofish (*Gambusia affinis*) as the test animal, Wallen et al. indicated that the 96-hour TL_m was greater than 56,000 mg/l, a concentration much larger than the solubility.

TVA has proposed no specific limits for calcium sulfate; however, the concentration is limited by the allowable sulfate concentration and the permissible added calcium hardness.

Sulfates

McKee and Wolf discuss sulfate content as follows.

> (a) Domestic Water Supplies. The 1962 Drinking Water Standards of the USPHS recommend that sulfates not exceed 250 mg/l, except where a more suitable supply is not available. This limit does not appear to be based on taste or physiological effects other than a laxative action toward new users. Public water supplies with sulfate contents above this limit are commonly and constantly used without adverse effects. The 1958 WHO International Standards established a "permissible limit" of 200 mg/l

and an "excessive limit" of 400 mg/1, but set no maximum allowable limit. The 1961 WHO European Standards include a recommended limit of 250 mg/1 for sulfates.

Korotchenok reported on heavily mineralized drinking waters in western Turkmenia (USSR), noting that no outbreaks of disease have been ascribed to waters in which the content of sulfate did not exceed 1295 mg/l. In British Somaliland well waters used for human consumption contain very high sulfates, many having 2000-3000 mg/l. One village is using water of 4400 mg/l sulfates. A survey in North Dakota indicated that water containing less than 600 mg/l of sulfates is usually safe. In reviewing the literature, Moore quotes Sollman to the effect that concentration of 1000 mg/l of sulfates in water is harmless. A cathartic dose is 1.0 to 2.0 grams, or a liter of water containing 1000 to 2000 mg/l of sulfates.

Sulfates appear to have no detrimental effect on the corrosion of brass fittings in domestic water systems, nor do concentrations less than 200 mg/l increase plumbosolvency.

Whipple is quoted by Moore to the effect that the taste thresholds of sulfate salts were as follows:

Sodium sulfate	200-500 mg/l
Calcium sulfate	250-900 mg/l
Magnesium sulfate	400-600 mg/l

(b) Industrial Water Supplies. Limiting or threshold concentrations, or optimum ranges, for sulfates are assembled below:

	Limits of recommended values, mg/l			
Industrial process	SO_4	$CaSO_4$	$MgSO_4$	Na_2SO_4
Brewing	-	100-500	100-200	100
Carb beverages	250	-	-	-
Concrete corrosion	25	-	-	-
Ice making	-	300	130-300	300
Milk industry	60	-	-	-
Photo processes	-	100	-	-
Sugar making	20	-	-	-
Textiles	100	-	-	-

TVA has proposed a limit of 150 milligrams per liter for sulfates to provide a reasonably satisfactory water for both domestic and industrial use. Normal water treatment has little effect on sulfate concentration.

Sulfite

The major concern in regard to high sulfite concentration is oxidation to sulfate, thus lowering the dissolved oxygen content of the receiving water.

Magnesium

The effect of dissolved magnesium has been treated by McKee and Wolf.

(a) Domestic Water Supplies. Magnesium is an essential mineral element for human beings; the daily requirement of magnesium is about 0.7 gram. Magnesium is considered relatively non-toxic to man and not a public health hazard because, before toxic concentrations are reached in water, the taste becomes quite unpleasant. At high concentrations, magnesium salts have a laxative effect, particularly upon new users, although the human body can develop a tolerance to magnesium over a period of time.

The 1946 USPHS Drinking Water Standards recommended a limit of 125 mg/l but there is no limit in the 1962 standards. The 1958 WHO International Standards have a "permissible limit" of 50 mg/l and an "excessive limit" of 150 mg/l, but no maximum allowable concentration. The 1961 WHO European Standards have a recommended limit of 125 mg/l, but if the sulfate exceeds 250 mg/l, the magnesium is limited to 30 mg/l.

The taste threshold for magnesium (in $MgSO_4$) has been reported as 100 mg/l and for the average individual it is given as about 500 mg/l.

The negative correlation between hardness in water and cardiovascular disease does not appear to hold for magnesium as it does for calcium; yet one investigator reports the favorable use of magnesium sulfate to treat such cases and claims that magnesium, rather than calcium, is the beneficial element in reducing cardiovascular attacks.

(e) Fish and Other Aquatic Life. The relative concentrations of magnesium and calcium in water may be one factor controlling the distribution of certain crustacean fishfood organisms, such as copepods, in streams. Hart et al. cite a report that among U.S. waters supporting a good fish fauna, ordinarily 5 percent have less than 3.5 mg/l of magnesium; 50 percent have less than 7 mg/l; and 95 percent have less than 14 mg/l.

Magnesium chloride and nitrate can be toxic to fish in distilled water or tap water at concentrations between 100 and 400 mg/l as magnesium. However, magnesium chloride, nitrate, and sulfate, at concentrations between 1000 and 3000 mg/l as magnesium have been tolerated for 2-11 days. Some fresh-water fish have been found in very saline lake water containing over 1000 mg/l of magnesium as well as additional sodium and calcium salts.

TVA has proposed no specific limit on magnesium.

POTENTIAL UTILIZATION OF SOLID WASTE FROM LIME/LIMESTONE WET-SCRUBBING OF FLUE GASES*

by

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INTRODUCTION

The increasing waste disposal problem associated with coal combustion may be compounded by the greater amount of waste generated if potential alkaline earth sulfur dioxide abatement systems are implemented. Although utilization schemes for normal flyash are available, "modified flyash," the solid by-product resulting from lime/limestone wet-scrubbing programs, represents a new type of solid waste material having different chemical and physical properties from regular flyash. In addition, simple disposal of this ash by land fill or lagooning may cause serious water pollution problems especially if dolomite is used as a modifying agent. Previous research(1) has shown that very little potential exists for mineral separation and beneficiation of this new ash and indicates that the most economical utilization scheme would involve total or whole utilization of the ash. For these reasons the Coal Research Bureau of West Virginia University has been performing research under partial support from EPA (Environmental Protection Agency)(2) to develop and evaluate total utilization processess. As a result of this research, several promising utilization areas have emerged. These include production of autoclaved materials such as calcium-silicate products, production of materials such as mineral wool using high temperature processes and agricultural uses such as soil amendments.

Sources of Modified Flyash

Several modified flyashes were investigated during the course of this research; however, only two were of a wet-collected nature. They were obtained from the Kansas Power and Light Co., Lawrence, Kansas (designated KPL), a limestone wet-scrubbing system, and from the Union Electric Company, St. Louis, Missouri (designated SLD), a dolomite wet-scrubbing system. In addition, a sample from the Shawnee Steam Plant, Paducah, Kentucky (designated TVA) was also examined. This ash originated from a limestone injection, dry-collection system of the type which could possibly be employed before a wet-scrubber.

Autoclaved Products

Because modified flyash liberates sorbed sulfur dioxide at elevated temperatures, it was necessary to find a technique for the total utilization of this ash which would either lock the sulfur into the product or require no external application of heat. Preliminary research examining the natural pozzolanic activity of limestone modified flyash indicated that some cementitious setting occurred. Such setting is sufficient to obstruct power plant process lines if water flow should stop but does not appear to impart enough strength for structural products. For this reason and because the technology has been well developed in Europe using normal flyash, autoclaving was selected for further investigation. In addition to forming a stronger material, this technique would also have the advantage of locking sulfur into the final product.

Various autoclaved products were investigated using modified ash as the principal raw material. Those products exhibiting the greatest potential for utilization of modified ash were:

a. brick or block,

b. aerated or foamed concrete, and

c. concrete materials.

A. Calcium-Silicate Brick

Calcium-silicate (CS) brick production was examined as a potential large tonnage application of limestone modified flyash. Bricks produced by autoclaving modified flyash have the added advantage of binding the sulfur components within a calcium-silicate matrix, and because they are full-strength after curing, they are immediately available for marketing. In addition, bricks made using this raw material surpass the standards for conventional sand-lime brick.

Figure 1 illustrates a simplified process flowsheet for the production of CS brick. As illustrated, this process involves dewatering of the ash, addition of silica sand and lime, mixing of the resultant material, pressing to the desired form, humidity curing and autoclaving. Brick made with, on a dry basis, 40 percent KPL wet collected limestone modified flyash, 39 percent silica sand (30 x 100 mesh) and 11 percent lime (95 percent pure CaO) exceed ASTM (C73-67, C73-51) standards for grade SW (severe weathering) calcium-silicate brick. The compressive breaking strengths are in excess of 5000 psi as compared to the ASTM specification of 4500 psi minimum.

Process parameters which were found to be of importance in the production of CS brick include mixing and humidity curing. It was found that surface cracking due to insufficient calcium-silicate bonding occurred if the various components were not intimately mixed before pressing. This problem was solved through the use of a muller-type mixer. Also, it was found that the compressive strength of the final product could be increased significantly if a humidity curing step was incorporated in the process prior to autoclaving. The humidity curing was effected by storing the pressed green brick over water at room temperatures for periods up to twelve hours.

Among the promising areas for utilization of calcium-silicate brick are: general low cost construction materials, interior walls, decorative walls, patios, and thermal or acoustic insulating walls or barriers.

B. Aerated Concrete

Originally patented in the U. S., aerated concrete has been widely developed in Europe. Practically all new factory buildings in Sweden and 80 percent in West Germany are constructed, in part, using this material.(3)

This lightweight structural material consists of small non-communicating gas cells entrained in a calcium-silicate matrix.

A process flowsheet for the production of aerated or foamed cellular concrete from modified flyash is included as Figure 2. Additions of cement and a gas producing agent to the ash are required; however, for this process, no pressing or humidity curing such as was required for brick production is necessary. Also, if a dry-collected modified ash is used, additional lime or sand is not required. On a dry basis the composition of materials used for aerated concrete production was 90 percent dry-collected modified ash, 10 percent portland cement (type I) and 0.16 percent aluminum powder.

The resulting aerated concrete has a density which may be varied from 50 to 56 lbs/ft^3 and a compressive strength, which may be controlled, between 400 and 850 psi. Commercial aerated concrete varies from 20-50 lbs/ft^3 in density and has compressive strengths on the order of 400-800 psi. This material can be sawn, nailed, drilled, screwed or glued as with wood but has the thermal and fire resistant properties of concrete. A few potential areas for utilization are in non-loadbearing walls, sandwich construction with brick or concrete for insulating purposes and interior surfacing for exterior walls. This material can be formed in desired shapes or cut from panels and should be highly suitable for modular construction.

Research in this area was performed using both wet and dry-collected modified ashes. Chemically very few elemental differences are apparent between the two types of ash; however, the greater amount of reactive lime in the dry-collected material made it more amenable than wet-collected material to this process. As with foreign manufacture which uses normal flyash, aeration and setting times are crucial in that setting must occur after aeratior is completed and before the entrained bubbles collapse. It is felt that a major advantage of modified flyash production may lie in the use of electrostatic precipitators in conjunction with wet scrubbers. A dry ash suitable for aerated concrete production would be obtained in large quantities while the overall efficiency of the sulfur dioxide abatement process would probably not be affected. Such a process would greatly reduce the need for ash dewatering and would act to reduce the potential threat of increased water pollution. In addition, a predominantly calcium sulfate material would be produced in the scrubber system.

C. Poured Concrete

The natural pozzolanic properties of limestone modified flyash indicated that a potential use might be as a cementing agent in concrete materials. Because research on CS brick production showed that autoclaving increased calcium-silicate bond formation, further research was performed to investigate the feasibility of using modified ash as the cementing agent for the production of concrete block.

Included as Figure 3 is the process flowsheet employed in this phase of research. It should be noted that the composition is the same as for CS brick with the exception that less dewatering is required. Also, it should be pointed out that the material is poured into molds instead of pressed. As with CS brick, this composition consisted, on a dry basis, of 50% wet-collected modified flyash, 39 percent silica sand (30 x 100 mesh) and 11 percent lime (95 percent CaO). The resulting poured concrete which is similar to concrete block had a bulk density of 90 lb/ft^3 as compared to 150 lbs/ft^3 for conventional concrete block and a compressive strength of approximately 900 psi as compared to 1000 psi for conventional block. Although addition of the necessary aggregate could raise the bulk density to 100 lb/ft^3, this would still be only 2/3 the bulk density of standard block. Storage requirements could also be reduced as this is a full strength, non-shrinking product out of the autoclave and does not require 3 to 4 weeks curing time before sale.

An advantage of the use of modified ash is that no prior grinding or crushing of the raw material is required. In addition, the possibility is being examined that limestone modified flyash could be used for the production of an autoclaved aggregate to be used as coarse material for this concrete.

The advantages of producing autoclaved calcium-silicate products from limestone modified flyash would include:

1. No sulfur dioxide capture or marketing problems would result as processing occurs below the temperature for sulfur dioxide regeneration;
2. Little or no storage or curing time is required before use as the structural materials produced are durable, pre-shrunk and pre-strengthened;
3. No exotic equipment is required for production as common European technology is employed;
4. No pollution problems should occur at the plant as rejects and process waters may be recycled; and
5. A potential large tonnage market exists in areas of low cost housing and construction.

Fired Products

High temperature processing was also examined to develop other possible uses for modified flyash, the most promising being mineral wool.(4) The alkaline earth constituents in limestone modified flyash reduce the amount of heat necessary to make the ash sufficiently fluid for the production of mineral wool. Comparative tests using normal flyash and bottom ash with equivalent amounts of lime added as a fluxing agent gave a poor grade of mineral wool and required more heat for processing. Conversely, mineral wool fibers produced from modified ashes were uniform, quite resilient and were superior to commercial fibers in protecting steel from rust corrosion.

As mentioned previously, the modified ash releases sorbed sulfur dioxide upon heating to temperatures over 1700°F. Since this could constitute a new air pollution problem, it was felt that a study of sulfur dioxide evolution from heated modified ash was in order. Accordingly, several modified flyashes, both wet and dry-collected, were examined to determine their sulfur evolution characteristics. In all instances, sulfur dioxide was evolved over a narrow temperature range in a relatively pure form and in concentrations similar to those considered suitable for sulfuric acid manufacture. For example, the theoretical total yield of sulfur dioxide in sample KPL is 10.34 percent by weight. At 2140°F, (melting temperature 2150-2160°F), 96 percent of its total yield is given off in twenty minutes. Even with this long heating period, concentrations of 9-13 percent sulfur dioxide in the off gas could be maintained. The only impurities observed were carbon dioxide and water vapor, both of which can be evolved at lower temperatures if desired.

After evolution of the sulfur gases, the parent ash may be further heated to a molten state for production of mineral wool or it may be cooled and utilized for the production of fired ceramic materials.

Soil Amendment

Dried sample KPL (wet-collected, limestone modified flyash) is being examined as a soil amendment agent. This work is currently being performed under sub-contract to Virginia Polytechnic Institute.* The results to date indicate that modified flyash with its increased calcareous components may find use as a soil amendment in the area of pH control. In addition, it was noted that such usage effects an increase in the boron supplying power of some soils to which the ash was added. As with regular flyash, modified ash also has the ability to improve the texture and drainage characteristics of some soils.

A potential advantage for wet-collected modified flyash is that the slurry may be sprayed directly on the soil area without the need for prior drying.

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*A report of this research, performed by Dr. David Martens, is included as an appendix in the final report of Contract No. CPA 70-66.

Before such utilization is recommended, however, further research will be necessary to determine whether a possible pollution problem due to water leaching occurs.

SUMMARY

Wet-collected modified flyash has been found to be a suitable raw material for the production of autoclaved structural products such as bricks, aerated concrete and cement materials. Other areas of application are in heat treating for mineral wool production and sulfur dioxide collection as well as in soil amendment for agricultural purposes. All of the processes discussed utilize the unique characteristics of modified flyash to eliminate a potential solid waste disposal problem. A more detailed discussion of the processes described in this paper may be found in the final report for Contract No. CPA 70-66 which will be available from the Environmental Protection Agency in the near future.

REFERENCES

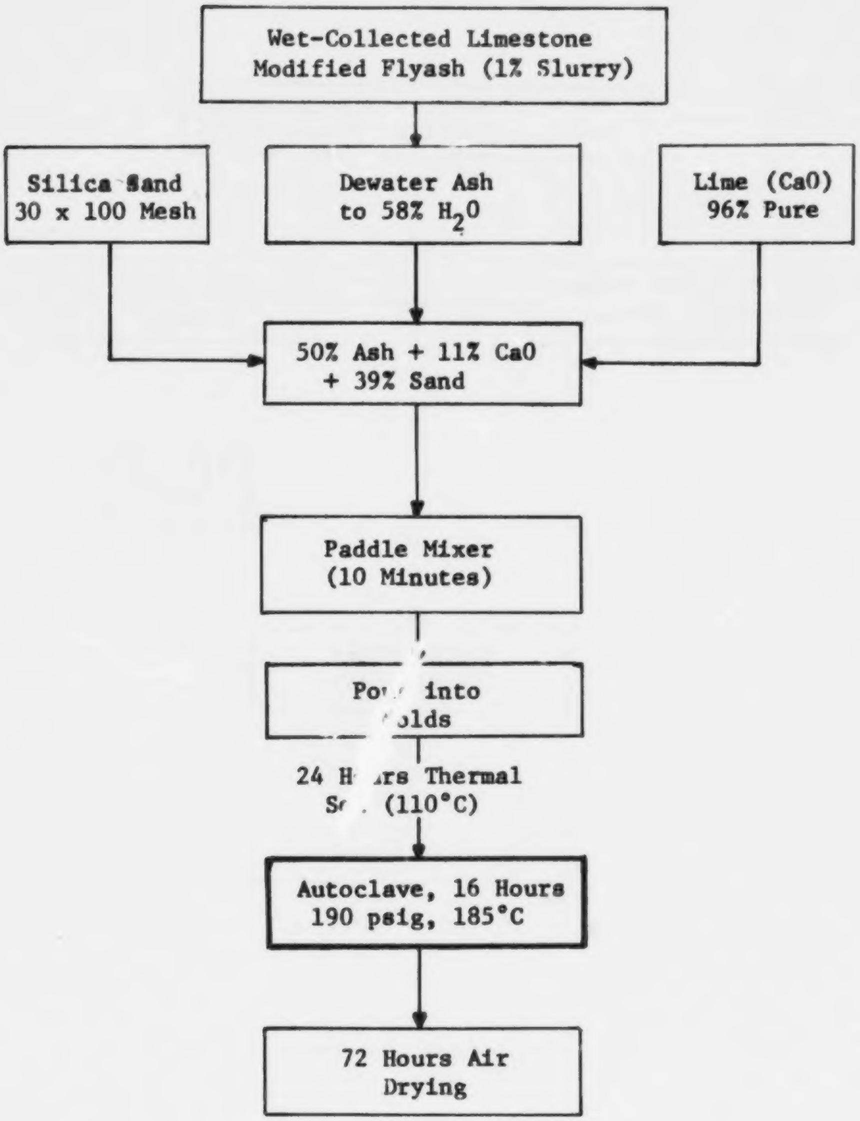
1. Anderson, Ronald E., Cockrell, Charles F., et al., "Study of Potential for Recovering Unreacted Lime From Limestone Modified Flyash by Agglomerate Flotation," Final Report, Contract PH 22-68-18, National Air Pollution Control Administration, May, 1970.

2. Contract numbers CPA 70-66 and EHS D 71-11 between West Virginia University and the Environmental Protection Agency.

3. ________, PFA Data Book, Central Electricity Generating Board, England (1969).

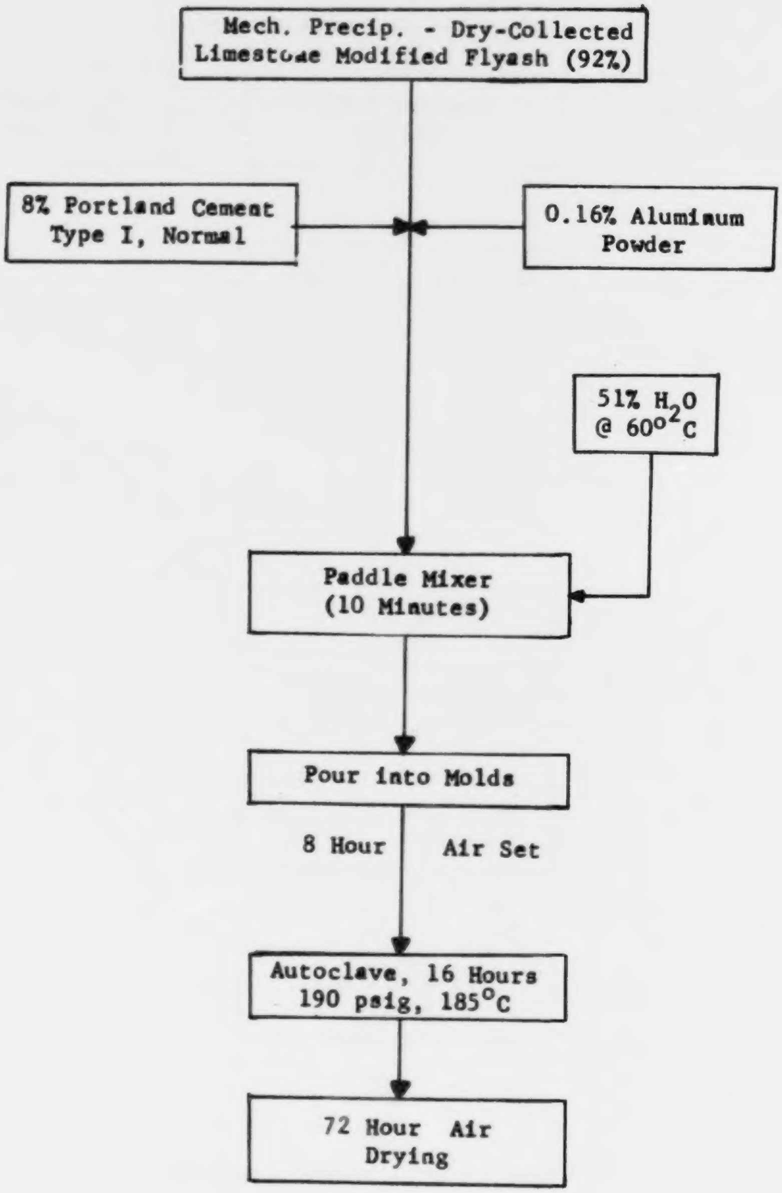
4. Cockrell, C. F., Muter, R. B., and Leonard, J. W., "Study of the Potential for Profitable Utilization of Pulverized Coal Flyash Modified by the Addition of Limestone-Dolomite Sulfur Dioxide Removal Additives," Final Report, Contract PH 86-67-122, National Air Pollution Control Administration, April, 1969.

FIGURE 1


Wet-Collected Limestone Modified Flyash (1% Slurry)
Silica Sand 30 x 100 Mesh
Dewater Ash to 58% H_2O
Lime (CaO) 96% Pure
50% Ash + 11% CaO + 39% Sand
Paddle Mixer (10 Minutes)
Pour into Molds
24 Hours Thermal Set. (110°C)
Autoclave, 16 Hours 190 psig, 185°C
72 Hours Air Drying

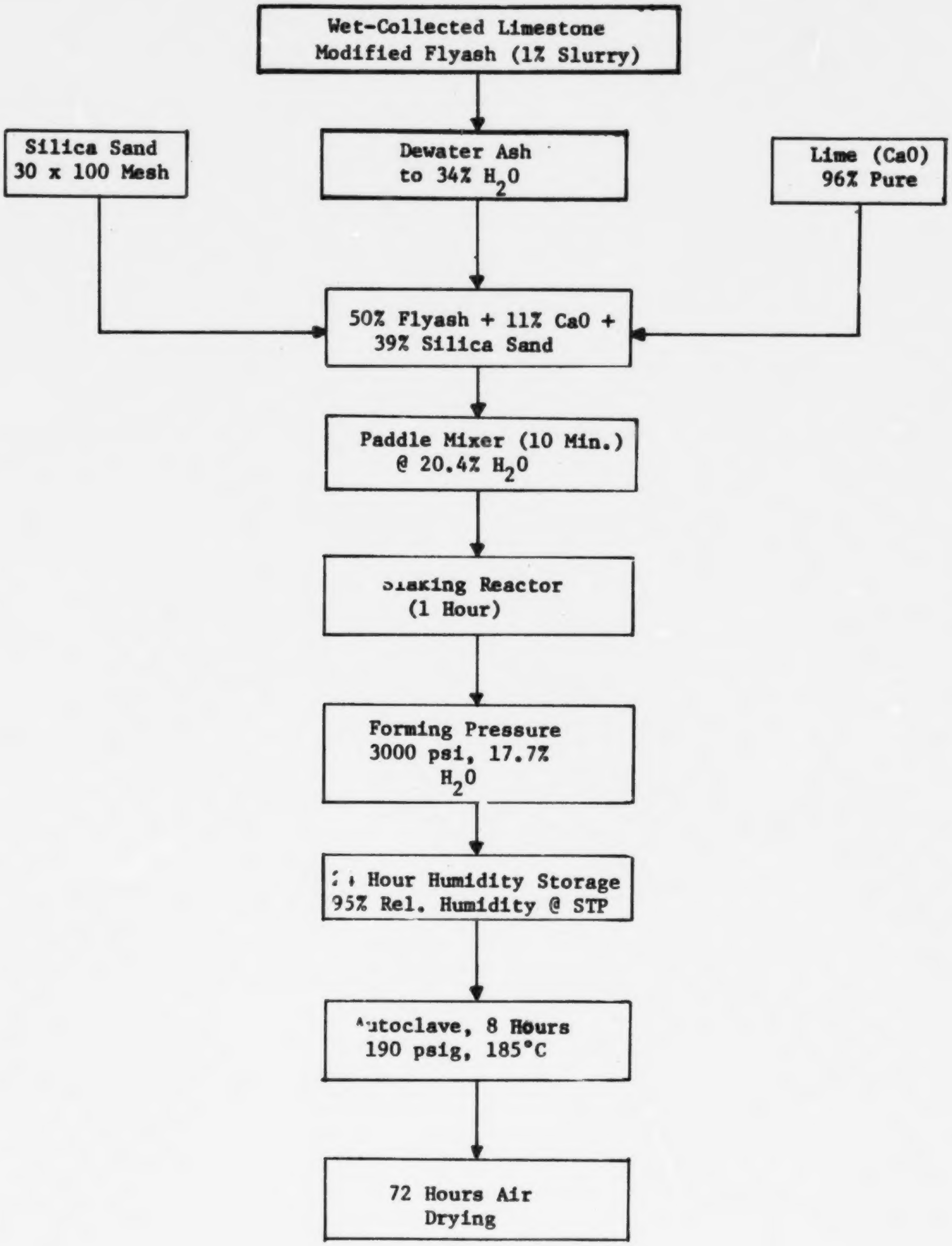
FLOW SHEET: FORMED CONCRETE

FIGURE 2


Mech. Precip. - Dry-Collected Limestone Modified Flyash (92%)
8% Portland Cement Type I, Normal
0.16% Aluminum Powder
51% H_2O @ 60°C
Paddle Mixer (10 Minutes)
Pour into Molds
8 Hour Air Set
Autoclave, 16 Hours 190 psig, 185°C
72 Hour Air Drying

FLOW SHEET: AERATED CONCRETE

FIGURE 3


Wet-Collected Limestone Modified Flyash (1% Slurry)
Silica Sand 30 x 100 Mesh
Dewater Ash to 34% H_2O
Lime (CaO) 96% Pure
50% Flyash + 11% CaO + 39% Silica Sand
Paddle Mixer (10 Min.) @ 20.4% H_2O
Slaking Reactor (1 Hour)
Forming Pressure 3000 psi, 17.7% H_2O
24 Hour Humidity Storage 95% Rel. Humidity @ STP
Autoclave, 8 Hours 190 psig, 185°C
72 Hours Air Drying

FLOW SHEET: CALCIUM-SILICATE BRICK

PILOT SCALE RESEARCH AND DEVELOPMENT

F.T. Princiotta, Chairman

Participants:

B.N. Murthy, D.B. Harris, and J.L. Phillips
I.S. Shah
R.A. Person, C.R. Allenbach, I.S. Shah, S.J. Sawyer
R.J. Gleason
T.M. Kelso, P.C. Williamson, J.J. Schultz
N.D. Moore
A. Saleem, D. Harrison, N. Sekhar
J.L. Shapiro and W.L. Kuo
J.H. McCarthy and J.J. Roosen
A.L. Plumley and M.R. Gogineni
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John M. Craig, Burke Bell, J.M. Fayadh
Robert J. Phillips
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Pilot Scale Research and Development

(Parts I, II, and III)

Second International Lime/Limestone Wet Scrubbing Symposium

New Orleans, Louisiana

November 8-12, 1971

F.T. Princiotta, Chairman

SUMMARY

In light of the recent trend toward preserving and improving man's environment, legislation and genuine public concern has put increasing pressure on electrical utilities to control the discharge of gaseous and particulate pollutants. Since wet limestone processes are generally considered closest to the state of the art in controlling sulfur oxide emissions, research and development has been particularly intense over the last several years in this area. The number of papers in this session and the depth of investigation supports the conclusion that more intensive and comprehensive investigation of wet limestone processes has occurred relatively recently.

The Pilot Scale Research and Development Session of the Second International Lime/Limestone Wet Scrubbing Symposium included papers which presented pilot plant results and pilot plant status for a variety of scrubber types. Emphasis has been noted in selection of scrubbers which are non-tortuous and not overly prone to scaling or plugging when handling saturated or supersaturated limestone or lime slurries. For the most part emphasis has also been on closed loop systems, which although are the most prone to reliability problems, are also the most acceptable since they minimize the extent of water pollution problems.

The participants in the Pilot Scale Session were as follows:

Name	Organization
B. N. Murthy	Environmental Protection Agency
I. S. Shah	Chemico
C. R. Allenbach	Union Carbide
R. J. Gleason	Cottrell Environmental Systems
T. M. Kelso	Tennessee Valley Authority
N. D. Moore	Tennessee Valley Authority
A. Saleem	Ontario Hydro
J. L. Shapiro	Bechtel
J. H. McCarthy	Detroit Edison
A. L. Plumley	Combustion Engineering
D. E. Reedy	Universal Oil Products
B. Bell	Zurn Environmental Engineers
R. J. Phillips	General Motors Technical Center
I. E. Campbell	Smelter Control Research Association

Tables 1 and 2 describe the pilot facilities and summarize results of selected pilot plant studies presented in the Pilot Scale Session. Please note, that only typical results were included in the table, since it was infeasible to include all results from all the units described. Also, the EPA Prototype Facility at the Shawnee Steam Plant and the Bischoff Prototype were included to show how these larger plants compare to the pilot scale unit in terms of size and scrubber types.

Also included were some selected pilot plant results from earlier studies by Howden-ICI in the 1930's and 1940's in order to help put the most recent results, as presented in the Pilot Scale Session, in reasonable perspective.

Scrubber types which have received the most attention have been the: venturi, Turbulent Contact Absorber, Hydrofilter (flooded marble bed), spray tower and packed tower. Generally, pilot plant results have indicated that under carefully selected operating conditions, all of these scrubbers, with the probable exception of the packed tower due its inherent plugging tendencies, can be operated with relatively high SO_2 and particulate removal efficiencies, with acceptable reliability. Pilot plant results have indicated that the desirable combination of good removal efficiencies without excessive down-time can be achieved, under the following conditions: (1) high liquid to gas flow rate ratios, (2) high solids content in the scrubber slurry, (3) long residence times in a delay tank following the scrubber and (4) proper selection of scrubber type.

Table 1. Selected Wet Limestone Pilot Plants and Prototype Facilities Status and Design Characteristics

Plant	Status	Design Characteristics				
		Size acfm	Alkali	Scrubber	Pt of Alkali Addition	Fuel
Howden - ICI (Fullham)	Tested in mid-1930's	3,150	Lime and limestone	Grid(wood)-packed	Scrubber circuit	Coal 1. 7-2. 0%S
Howden - ICI (Bankside)	Tested 1948-49	11,700	Whiting chalk (limestone) and lime	Grid(wood)-packed	Scrubber circuit	Oil 2. 7%S
EPA/Zurn at Key West and Shawnee Steam Plant (Mobile Unit)	Tested 1970-71	1,500	Various limestone and lime	Inspirating type; Zurn Dustraxtor	Scrubber circuit	Oil (1-2%S) at Key West; coal (1. 5-3%S) at Shawnee
Bischoff Scrubber Prototype at Steag Power Plant, Lunen, W. Germany	Started Feb 1971	110,000	Lime and calcium hydroxide	Venturi in series with spray tower	Gas inlet duct	Coal 2-4. 5%S
Ontario-Hydro	Tested 1971	4,000	Limestone	Spray tower	Scrubber circuit	Coal 1020-1600 ppm SO_2 inlet
Cottrell unit at Ohio Power's Tidd Plant	Tested 1970-71	1,000	Limestone	Venturi in series with a wetted film packed bed	Scrubber circuit (also some simulated boiler injection)	Coal 1100-2000 ppm SO_2 inlet

Table 1 (Cont.). Selected Wet Limestone Pilot Plants and Prototype Facilities Status and Design Characteristics

		Design Characteristics				
Plant	Status	Size acfm	Alkali	Scrubber	Pt of Alkali Addition	Fuel
TVA Unit at the Colbert Steam Plant	Tested 1971	2,600	Primarily limestone	1) Venturi-rod/ packed bed; 2) venturi-rod/ spray tower; 3) 3-stage TCA (mobile bed) scrubber	Scrubber circuit	Coal, 3000 ppm SO_2 inlet, 4g/scf part.
C. E. Prototype Facility at Windsor, Conn.	Started up 4/70; tests run for various customers and in-house tests since; currently EPA boiler calcined limestone tests start 12/6/71	12,000	Na_2CO_3, lime, limestone, dolomite	Hydrofilter (flooded marble bed) 1 or 2 beds	a) Scrubber circuit; b) boiler injection (simulated)	Oil (SO_2, fly-ash added)
Mohave/Navajo Pilot Facility	Started up 7/71; no data available due to pilot plant problems	two 4,000 circuits	Limestone, lime, soda ash (w/ and w/o regen. by lime)	1) TCA; 2) venturi; 3) polygrid packed; 4) Lurgi impingement	Scrubber circuit	Coal 0.3-0.8%S
EPA Prototype Facility at Shawnee Steam Plant	Testing sched. start 3/72	three 30,000 circuits	Limestone and hydrated lime	1) Venturi-spray or packed bed; 2) versatile TCA; 3) hydrofilter (marble flooded bed)	a) Scrubber circuit; b) boiler injection	Coal 1.5-3%S

Table 2. Selected Wet Limestone Pilot Plants and Prototype Facilities
Typical Performance and Operating Parameters

Plant	Typical Performance			Operating Parameters		Comments
	SO_2 Removal, %	Particulate Removal, %	Stoich. %	L/G gpm/1000 cfm	ΔP in. H_2O	
Howden - ICI (Fullham)	97-99	97-99	100 lime; 130 limestone	97	1.2	Scaling was a major problem, but design changes enabled fair operating reliability; L/G and scrubber size excessive by modern standards.
Howden - ICI (Bankside)	90-99	approx 98	110	138	5.7	Reliable operation a continuous problem; Settling difficulties encountered; L/G and scrubber size excessive by modern standards.
EPA/Zurn at Key West and Shawnee Steam Plant (Mobile Unit)	70	Not measured	100 limestone	Approx 600 (induced by scrubber)	12	Open-loop system; Results shown for fresh water--salt water slurry SO_2 removal approx 80%; Operating reliability good.
Bischoff Scrubber Prototype at Steag Power Plant, Lünen, W. Germany	89	99.7	110	--	10 (in venturi)	Large prototype system; Early results indicate scaling and plugging problems and mechanical difficulties; System is down now; to be restarted in early 1972.

Table 2 (Cont.). Selected Wet Limestone Pilot Plants and Prototype Facilities Typical Performance and Operating Parameters

	Typical Performance			Operating Parameters		
Plant	SO_2 Removal, %	Particulate Removal, %	Stoich. %	L/G gpm/1000 cfm	ΔP in. H_2O	Comments
Ontario Hydro	72	No part. in flue gas	130	72	0.5-1	Reliability of operation has been good; No serious scaling or plugging problems.
Cottrell Unit at Ohio Power's Tidd Plant	55-98	Not measured	100-120	40	7-9 (total)	Performance data based on an 80-hour test; some SO_2 variation due to SO_2 inlet variation; Considerable plugging of packed bed: 23 lbs after 80 hours.
TVA Unit at the Colbert Steam Plant[a]	1) Varied due to scaling; 2) 77 (avg); 3) 92 (avg).	1) 99.3; 2) 98.9-99.3; 3) 98.3.	1) 150; 2) 150; 3) 150.	1) 40; 2) 60 (to both); 3) 38.	1) Approx 10 (total); 2) 16 (total); 3) 9.	1) Major scaling in packed bed--deemed unacceptable; 2) A 354-hour test was run with only 20 hours down time--reliability good--only minor scaling; 3) A 172-hour test indicated no scaling problems--ball wear, grid erosion, and particulate entrainment were problems.
C.E. Prototype Facility at Windsor, Conn.	95+ (Na_2CO_3 1 bed); 80 (reliably with $CaCO_3$ and $Ca(OH)_2$ 2 beds)	99	100-110 (Na_2CO_3, $Ca(OH)_2$); 120-150 ($CaCO_3$)	15 (Na_2CO_3); 20 per bed ($CaCO_3$, $Ca(OH)_2$)	Approx 6 (per bed)	Unit designed to solve field unit problems and to predict performance of new units.

Table 2 (Cont.). Selected Wet Limestone Pilot Plants and Prototype Facilities Typical Performance and Operating Parameters

Plant	Typical Performance			Operating Parameters		Comments
	SO_2 Removal, %	Particulate Removal, %	Stoich. %	L/G gpm/1000 cfm	ΔP in. H_2O	
Mohave/Navajo Pilot Facility	--	--	--	--	--	Plant aimed at evaluating scrubbing of low SO_2 level flue gas; Plant versatile with extensive instrumentation; Plant to evaluate use of soda ash scrubber solutions with lime regeneration; Data should be available within several months.
EPA prototype Facility at Shawnee Steam Plant	--	--	--	--	--	Most versatile wet limestone facility; Extensive instrumentation; Tests are planned to fully characterize wet limestone scrubbing--break-in, screening, and long-term tests are scheduled; Unit to start up 3/72.

[a] Numbers listed opposite TVA Unit at the Colbert Steam Plant represent:
1) venturi-rod/packed bed;
2) venturi-rod/spray tower; and
3) three-stage TCA (mobile bed) scrubber.

SULFUR DIOXIDE ABSORPTION STUDIES WITH EPA IN-HOUSE PILOT SCALE VENTURI SCRUBBER

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SULFUR DIOXIDE ABSORPTION STUDIES WITH EPA IN-HOUSE PILOT-SCALE VENTURI SCRUBBER

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and

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The in-house venturi pilot plant system which was originally designed and in use for particulate removal studies, was modified to investigate the limestone wet-scrubbing process for sulfur dioxide removal. Changes included replacement of ductwork with fiberglass-plastic piping, installation of slurry mixing and hold tanks and clarifiers and instrumentation for measuring pH values, liquid and gas flow rates, slurry sampling, and for gas analysis. The venturi section was replaced by a stainless steel unit of similar dimensions and modified flow nozzle.

Vapor-liquid and solid-liquid mass transfer in the venturi scrubber were studied by treating flue gas containing sulfur dioxide with water, sodium hydroxide solution and limestone slurry in separate seriesof experiments. The results indicated that the venturi scrubber alone is not an efficient SO_2 absorption device. Liquid flow rate and liquid composition had an appreciable effect on the overall mass transfer coefficient, indicating that the liquid phase reaction was significant under the experimental conditions. Experiments with limestone slurry indicated some solid-liquid mass transfer in the venturi scrubber. Calcined limestone-flyash mixture removed more sulfur dioxide in the wet-scrubber than limestone.

The in-house venturi pilot plant studies also enabled the development of suitable methods for slurry sampling and evaluation of laboratory analytical methods for practical application in scrubber development.

SULFUR DIOXIDE ABSORPTION STUDIES WITH EPA IN-HOUSE PILOT SCALE VENTURI SCRUBBER

The limestone wet scrubbing process for sulfur dioxide absorption will be studied on a large scale by EPA early in 1972 using three pilot plants on a coal fired power generating station. The venturi scrubber is one of the three systems planned for investigations.

To study the important process variables in preparation for the large scale test plans, an existing EPA in-house venturi pilot plant which was in use for particulate removal studies, was modified. The main objectives of this study were:

(1) To determine the extent of vapor-liquid and solid-liquid mass transfer in the venturi scrubber.

(2) To investigate the factors influencing the important mass transfer steps in the scrubber.

(3) To gather preliminary information on the absorption of NO_x.

(4) To develop practical sampling and analytical methods for the prototype studies through trials under the pilot plant conditions.

EQUIPMENT

A flow diagram of the modified pilot plant system is shown in Figure 1. The major changes in the equipment consisted of the following:

(1) The venturi scrubber, de-entrainer and the cyclone were replaced with those of 304 stainless steel.

(2) The flow nozzle in the venturi was fitted with a 45° solid cone, to handle slurry feed. The dimensions of the venturi scrubber are shown in Figure 2.

(3) The ductwork downstream from the venturi up to the induced draft fan was constructed of 8 in. diameter fiberglas reinforced plastic pipe.

(4) The I.D. fan was coated inside with a corrosion resistant paint.

(5) Two 55 gallon capacity sealed hold tanks fitted with stirrers and inlet-outlet connections were installed in the slurry recycle line.

(6) A rectangular clarifier of 450 gallon capacity was added to the system to treat the slurry.

OPERATION AND ANALYSIS

Flue gas, produced by burning natural gas in an incinerator, was diluted with excess air to make up for the required volumetric flow rate through the scrubber. The temperature and humidity of the gas could be adjusted by prespraying with water in the incinerator. SO_2, NO and NO_2 were metered into the flue gas stream before the mixer, which was a dry venturi. The limestone or other dry solids were added to the flue gas at this point. The gas stream then entered the venturi scrubber where it was mixed with the liquid reagent. Downstream from the scrubber, the entrained liquid and particulates were removed in a knock-out drum followed by a cyclone from where the gas was discharged to the atmosphere through the I.D. fan.

Gas Sampling:

A Semi-automatic sampling system was constructed to monitor the flue gas composition at several points in the pilot plant. The sampling train included a glass cyclone to remove entrained particulates and droplets.

Flue Gas Flow Measurement:

An ASME standard venturi gas flow meter was used to measure the gas flow rate through the scrubber with an estimated accuracy within ±5%. The flow venturi was located in a straight run of duct following the I.D. fan.

Liquid and Slurry Flow Controls:

Standard venturi flowmeters were connected to L&N differential pressure cells and continuous recorders to measure liquid and slurry flow rates. The recorder-chart readings were used to manually control the flow rates.

Liquid and Slurry Sampling:

Sampling points at several points in the slurry flow system were connected to 1/4 and 1/2 inch stainless steel tubings for sample draw out. Care was taken during sampling to prevent oxidation or reaction with atmospheric carbon dioxide.

Solid-Liquid Separation During Slurry Sampling:

Laboratory tests with a continuous centrifuge had demonstrated that calcium carbonate particles could be rapidly separated from a slurry of similar composition as expected in a scrubber, before analysis to determine the rate of precipitation and dissolution in the system. However, under the pilot scale scrubbing conditions in which the slurry contained fly ash and calcined limestone particles, the performance of the centrifuge was not satisfactory. The outlet liquid stream would become cloudy with suspended particles and the flow lines in the centrifuge plugged with solids. Further work in developing a satisfactory alternate method of solid-liquid separation has progressed elsewhere.(2)

Gas Analysis:

SO_2 and NO_x were analyzed by Whittaker Analyzers which were calibrated with Span gases supplied in cylinders. The instrument output was connected to a continuous recorder.

O_2 and CO_2 were analyzed by a laboratory gas chromatograph. Sampling was done by the use of plastic bags.

Liquid & Slurry Analysis:

Sulfite in the liquid sample was analyzed immediately by a modified iodine method in which the pH of the solution was kept at 6.0-6.2 to prevent interference from nitrites. The iodine solution was generated as needed for each determination using standard iodate and excess iodide ion at low pH. The excess iodine was back-titrated with arsenite solution using a dead-stop technique for end point detection.

Samples were shipped under stable conditions and analyzed at Radian Laboratories for the following species:

carbonate
total sulfur as sulfate
total nitrogen
Ca
Mg
Na
K
Cl

The methods used for analysis are described in Reference 2.

RESULTS AND DISCUSSION:

Experiments were conducted in two series. In the first series, the vapor liquid mass transfer efficiency of the scrubber for sulfur dioxide absorption was studied by using only water and sodium hydroxide solution as reagents to circumvent problems of solids dissolving or precipitating in the scrubber. The concentration of sodium hydroxide was in the range of the dissolved reagent concentration in the wet-limestone scrubbing process. The experimental conditions are shown in Table 1.

The effect of operating variables on the mass-transfer efficiency was determined by calculating relative values of 'K_ga' the product of SO_2 mass transfer coefficient and the interfacial area, from the familiar expression for dilute gas concentration:

$$z = \frac{\overline{G}}{K_g a} \cdot \int_{Y\ out}^{Y\ in} \frac{dy}{y - y^*} = \frac{\overline{G}}{K_g a} \cdot N_t$$

TABLE 1

CONDTIONS FOR SERIES 1

FLUE GAS:				
FLOW RATE	(ACFM)	1000	TO	1300
TEMPERATURE	(^{o}F)	250	TO	325
COMPOSITION	(MOLE %)			
SO_2		0.20		
NO		0	&	0.045
NO_2		0	&	0.005
CO_2		0.3	TO	1.3
O_2		20		
H_2O		0.6	TO	4.2
N_2		BALANCE		
SCRUBBING REAGENT:				
NaOH IN WATER	(G MOLES/L)	0	TO	0.04
FLOW RATE	(GPM)	10	TO	15
SCRUBBER PRESSURE DROP:	(IN. H_2O)	7.8	TO	12.6

K_g = overall mass transfer coefficient for SO_2

a = gas-liquid interfacial area per unit volume,

y = gas phase SO_2 concentration

y* = gas concentration in equilibrium with the liquid

$\bar{G}$ = Average Molar gas flow rate through the scrubber

z = length of the scrubber

N_t = Number of transfer units

Relative value of $K_g a$ is then calculated as:

$$(K_g a)\ \text{rel} = \frac{K_g a}{(K_g a)\ \text{ref}} = \frac{N_t}{(N_t)\ \text{ref}} \times \frac{\bar{G}}{(\bar{G})\ \text{ref}}$$

Equilibrium gas concentrations were calculated from liquid concentrations, using a computer program. Experimental results (Table 2) indicated that sulfur dioxide absorption did not reach equilibrium with the venturi scrubber.

Figure 3 shows the effect of liquid composition on Kga. The strong dependence the rate of sulfur dioxide absorption on the liquid composition indicates that liquid film resistance in the venturi scrubber is significant in the concentration range studied.

The effect of gas and liquid flow rates on $K_g a$ is shown in Figure 4. The increase in mass transfer with liquid flow rate is expected to be due to increase in surface area from the additional droplets. An increase in gas flow rate did not appear to have an appreciable effect on mass transfer.

The pressure drop across the scrubber, however, was affected more by gas flowrate than the liquid flow rate (Figure 5). These results suggest that vapor-liquid mass transfer in the venturi scrubber can be increased without appreciabl power input by increasing the liquid flow rate for the same gas flow rate.

Figure 6 shows the effect of flue gas temperature on the absorption rates for water and alkali solution. Comparison of the results indicate that while a decrease in temperature increased absorption with water, an increase in temperature increased the absorption rate when the alkali solution was used. This indicates that alkali absorption in the scrubber is controlled by the chemical reaction mechanism in the liquid phase, since chemical reaction rate is a strong function of temperature. However, under process conditions when the equilibrium partial pressure of SO_2 is not zero, a lower temperature may favor absorption. Further studies are needed before firm conclusions on the effect of scrubber temperature on absorption rate can be made.

TABLE 2

EXPERIMENTAL RESULTS - SERIES 1

RUN NO.	INLET FLUE GAS FLOW RATE (ACFM)	TEMP. (O_F)	COMPOSITION, MOLE % SO_2	NO_x	CO_2	O_2	H_2O	AQUEOUS FEED NaOH Moles/1	Feed Rate (GPM)	SCRUBBER Δ P ($11_{H_2}0$)	SO_2 OUT (MOLE %) EXPERIMENTAL	EQUILIBRIUM
1	1040	300	.198	0	.85	19.6	2.4	0	10	8.75	.1645	.1210
1 A	1090	320	.200	0	.6	20.6	2.3	0	10	8.6	.1630	.1260
2	1020	310	.211	.054	1.2	17.7	4.0	0	10	7.8	.1780	.097
3	1230	315	.205	.056	.9	19.6	2.5	0	10	12.0	.1500	.111
3 A	1210	300	.199	.051	.4	18.8	2.3	0	10	11.4	.1560	.095
3 B	1210	300	.290	.05	--	--	--	0	10	12.6	.2460	.228
4	1010	310	.206	.044	1.3	18.8	2.5	0	15	9.0	.1570	.090
5	1010	260	.197	.039	.6	20.1	4.2	0	10	8.5	.1590	.086
6	1070	310	.200	.044	1.1	19.8	2.5	.0282	10	8.4	.0850	0
6 A	1120	300	.196	.05	--	--	--	.0416	9.9	9.3	.0850	0
7	1050	310	.198	.051	.7	19.2	2.7	.0365	15	9.2	.0460	0
8	1270	325	.246	.049	.5	20.1	1.6	.0370	10	12.4	.1475	0
8 A	1255	300	.202	.05	--	--	--	.0349	9.9	12.4	.0980	0
9	1060	260	.239	.048	.3	19.8	1.2	.0393	10	10.6	.1475	0
9 A	1115	250	.200	.05	--	--	--	.0280	10	9.5	.1100	0
10	1090	315	.239	.038	.10	19.2	.6	.0190	10	8.6	.1580	0
10 A	1100	300	.207	.05	--	--	--	.0116	9.7	8.7	.1420	.0775

TABLE 3

CONDITIONS FOR SERIES 2

FLUE GAS:

Flow Rate	1000 ACFM
Temperature	300° F

Composition (Mole %):

SO_2	NO	NO_2	CO_2	O_2	H_2O	N_2
0.20	0.045	0.005	0.8	20	1.0	BALANCE

SOLIDS:

Feed Rate: 150% Stoichiometric

Type:	Piqua Limestone	Piqua Limestone	TVA Calcined Limestone Flyash
	(1)	(2)	(3)
Composition:	86% $CaCO_3$	86% $CaCO_3$	35.2% as CaO
Particle Size: (Microns) Range:	2.0-50	2.0-32	2.0-40.3
Median:	15.5	12.7	6.5

LIQUID:

Flow Rate Trough Scrubber: 10 GPM

Composition: Saturated Liquid from Clarifier

Pressure Drop ("H_2O): 7.0-8.5

NO_x Absorption: No absorption of NO_x was noticed from the gas phase analysis since the change in NO_x concentration was within the range of instrumental error. Liquid phase analyses also did not indicate any significant absorption of NO_x.

Oxidation of absorbed SO_2 to sulfate was uniformly 10 percent in all the runs. Since the absorption rate of SO_2 was considerably more (about 4 times) with the alkali solution than with water, the rate of oxidation was proportional to the concentration of the sulfite in the liquid phase, indicating a chemical reaction or a liquid film mass transfer controlled mechanism for oxygen transfer in the scrubber. However, the concentration of oxygen in a power plant flue gas will be considerably less than that in these tests, and the same oxidation conditions may not apply to the prototype scrubbing conditions.

The extent of solid-liquid mass transfer in the venturi scrubber was qualitatively studied in the second series of experiments. Commercial grade limestone and calcined limestone-flyash mixture from dry limestone injection studies at Shawnee (TVA) were used to compare the effect of limestone type and composition on flue gas sulfur dioxide removal. The experimental conditions are shown in Table 3.

Three modes of operation were used to study the mass-transfer effects. In the first mode, clear saturated liquor from the clarifier was fed to the scrubber with solids injection, under steady state conditions. In the second mode, solids injection was suddenly stopped and gas monitoring continued. The difference in sulfur dioxide removal between the first and the second mode indicated whether any of the solids were hydrated in the scrubber. In the third mode of operation, with the system under steady state conditions as in the first mode, solids injection was suddenly stopped and the slurry from the hold tanks was directly fed to the scrubber, bypassing the clarifier. The difference in sulfur dioxide absorption between the first and the third mode of operation indicated whether any hydrated solids were dissolved in the scrubber.

The results, shown in Figure 7, indicate that very little hydration and dissolution of limestone or flyash-calcined limestone takes place in the venturi scrubber. The calcined limestone-flyash mixture removed appreciably more sulfur dioxide from the flue gas than limestone alone. The results also indicate that the limestone particle size had a minor effect on the sulfur dioxide absorption in the size range studied.

CONCLUSIONS:

The results of this investigation lead us to the following conclusions:

(1) The venturi scrubber alone is not an effective device for sulfur-dioxide removal from power plant flue gases.

(2) Liquid recirculation rate and composition have an appreciable effect on the rate of sulfur dioxide absorption in the venturi scrubber.

(3) Further work is needed to establish the effects of flue gas temperature and composition on the effectiveness of the scrubber.

(4) Negligible hydration and dissolution of the solids take place in the venturi scrubber.

(5) Limestone type, particle size and composition have considerable effect on sulfur dioxide absorption in the venturi. Detailed studies are needed to optimize the conditions.

REFERENCES:

1. Technical Note 200-006-19, "Evaluation of Sampling Procedures for Limestone-Wet Scrubbing Systems - Colbert Test Series", by Radian Corporation, Austin, Texas
2. Technical Notes 200-004-03 to 09, Radian Corporation
3. Final Report for EPA Contract No. CPA 22-69-138, by Radian Corporation

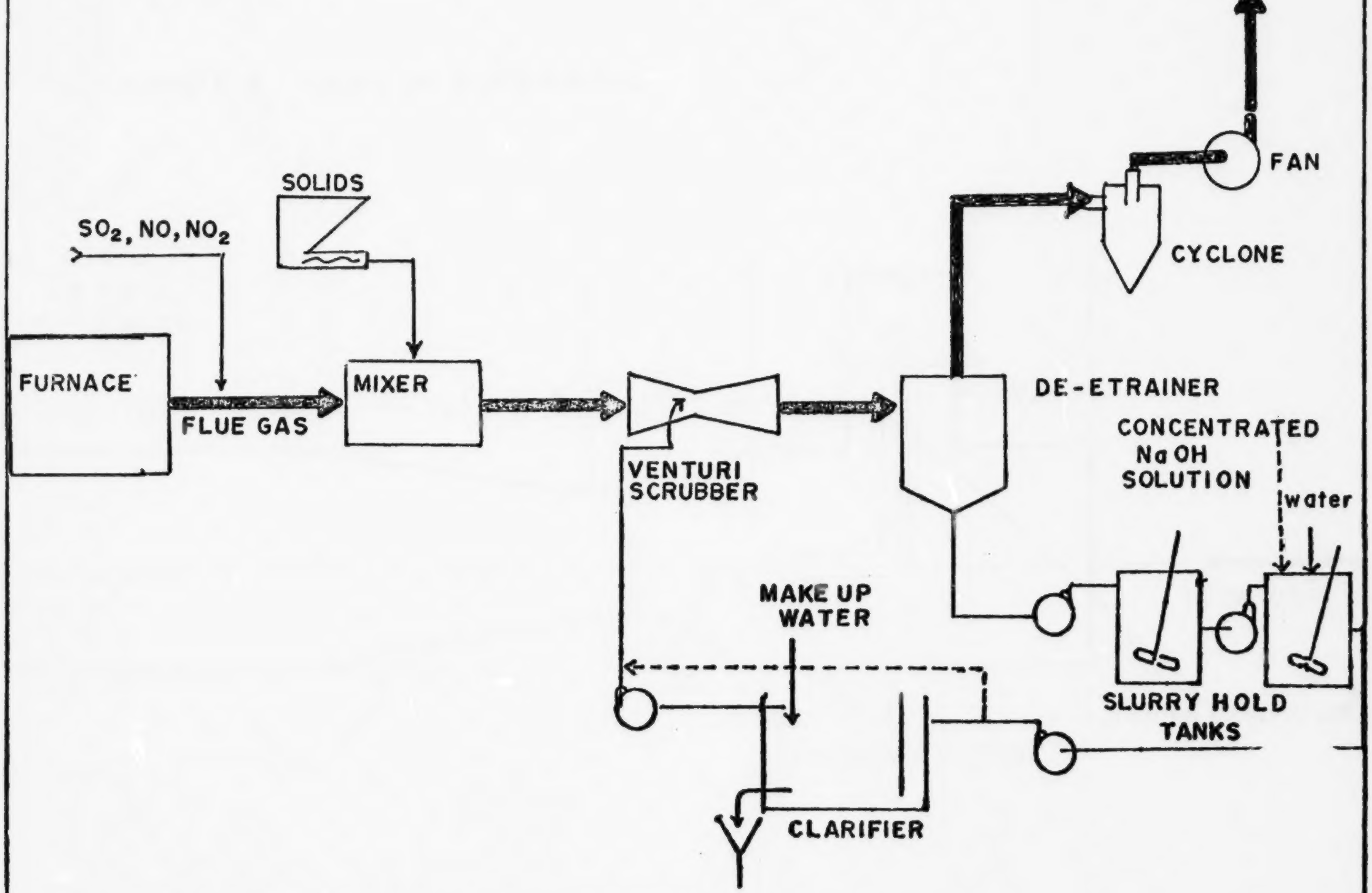


FIGURE I VENTURI SCRUBBER SYSTEM

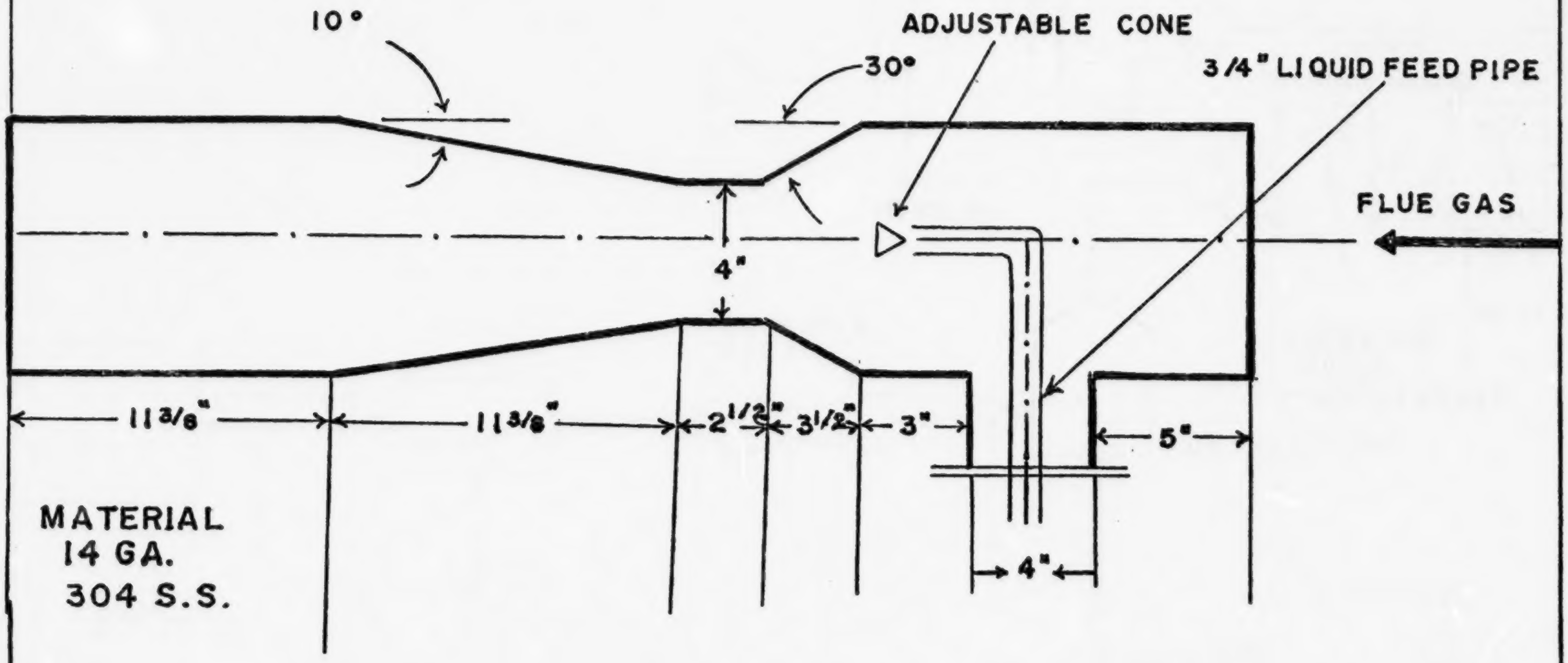


FIGURE 2 VENTURI DIMENSIONS

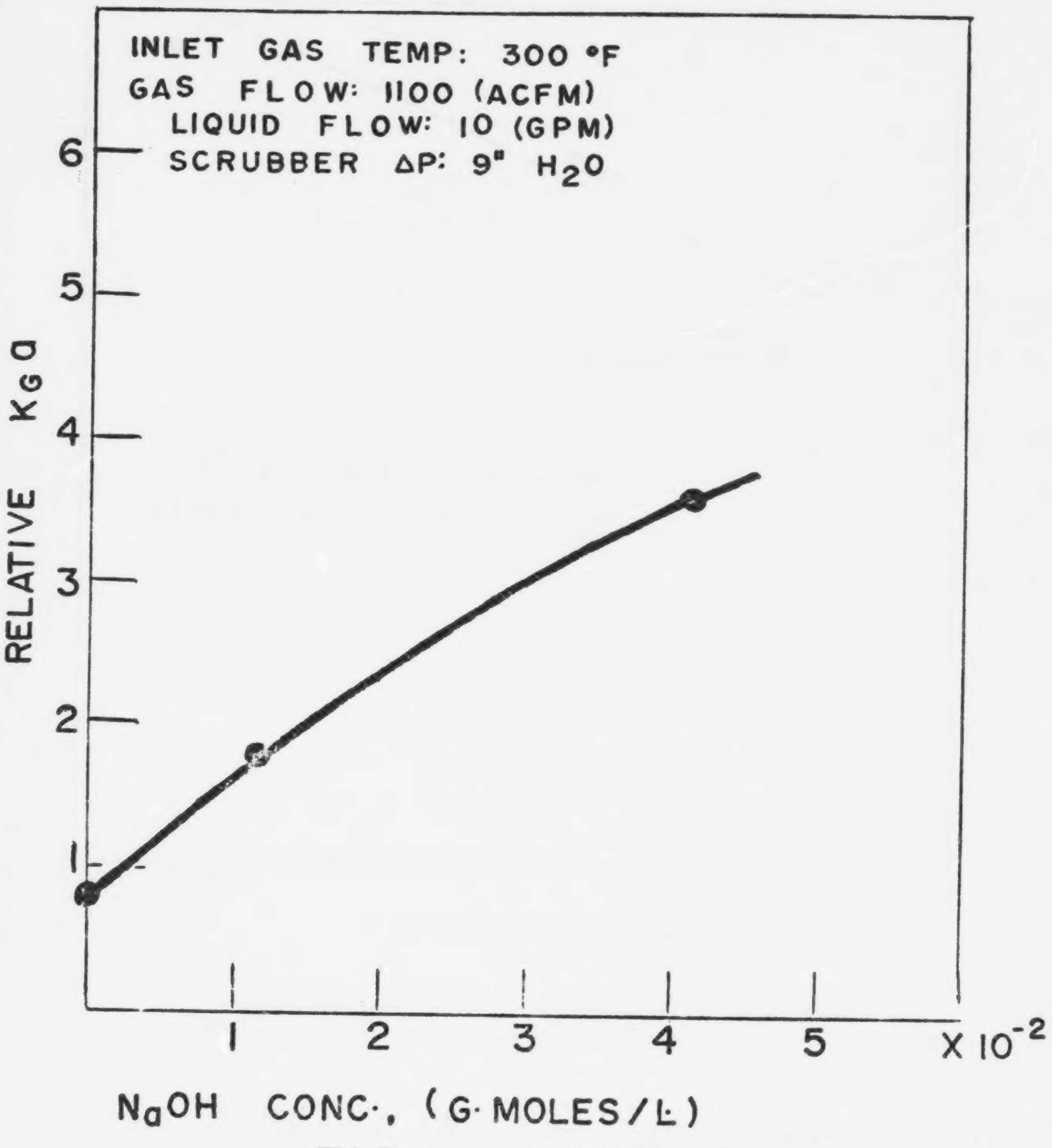
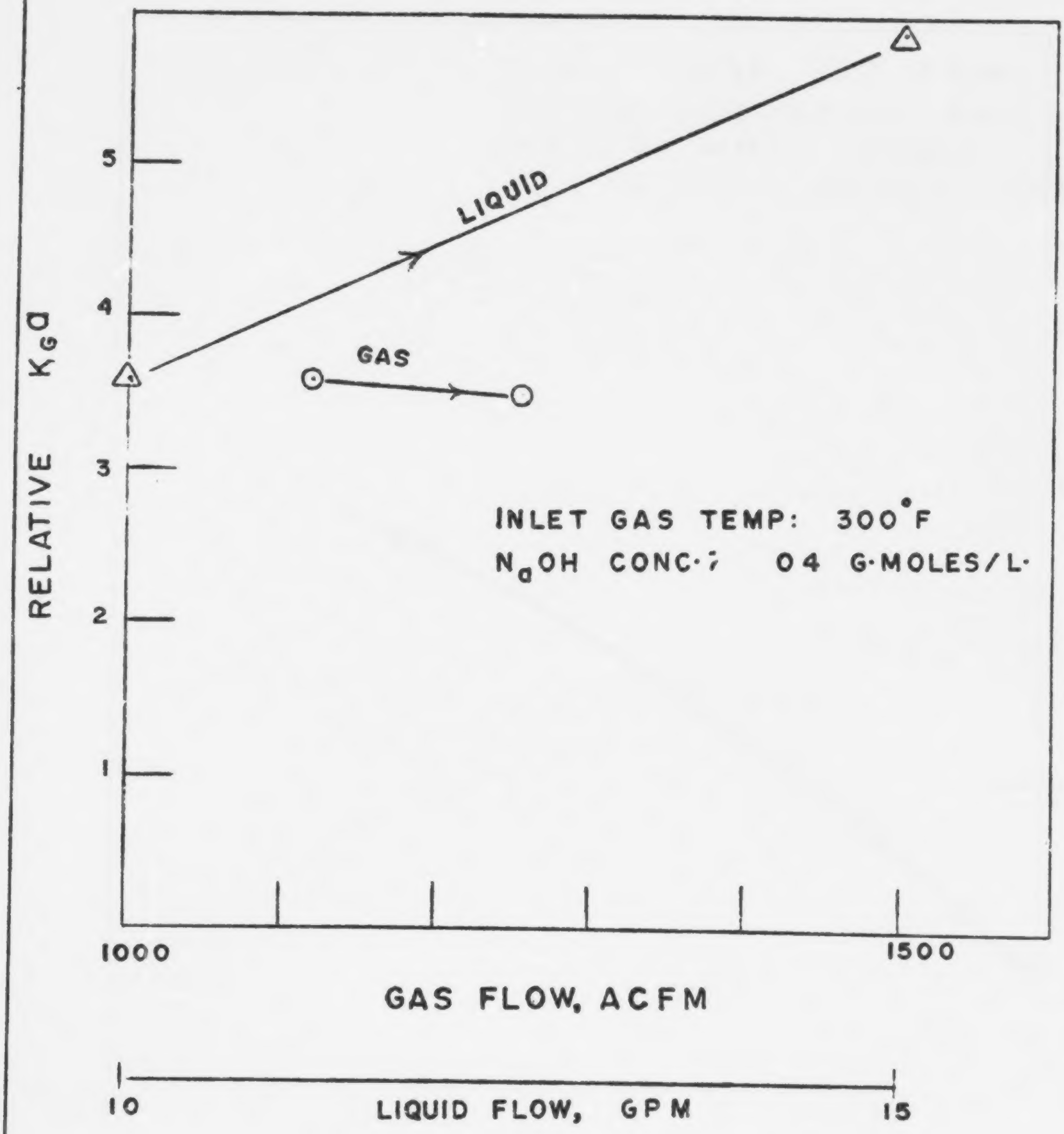


FIG. 3 EFFECT OF LIQUID COMPOSITION ON SCRUBBING



FIG· 4· EFFECT OF GAS AND LIQUID FLOW RATES ON $K_G a$

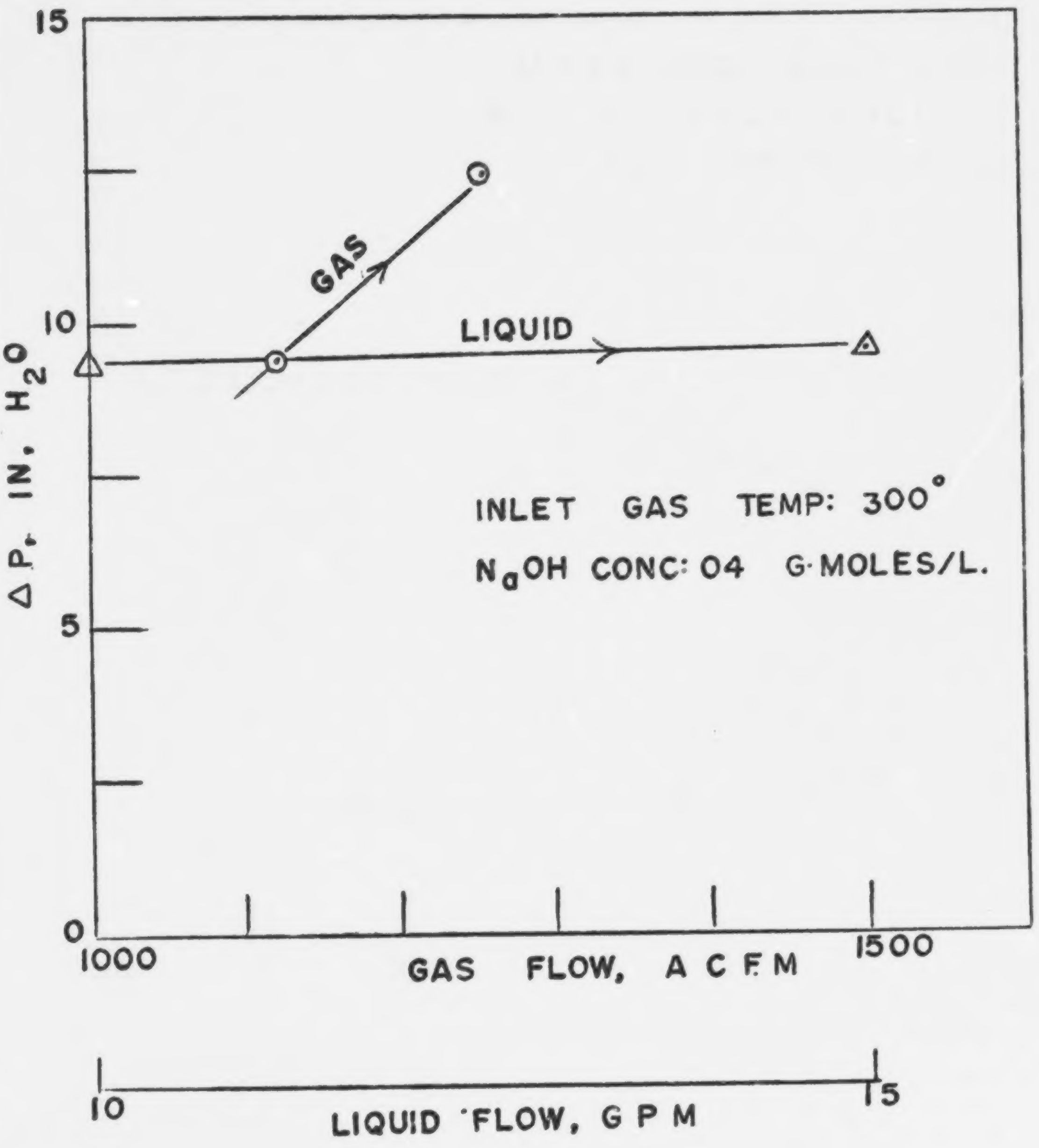


FIG. 5. EFFECT OF GAS AND LIQUID FLOW RATES ON ΔP

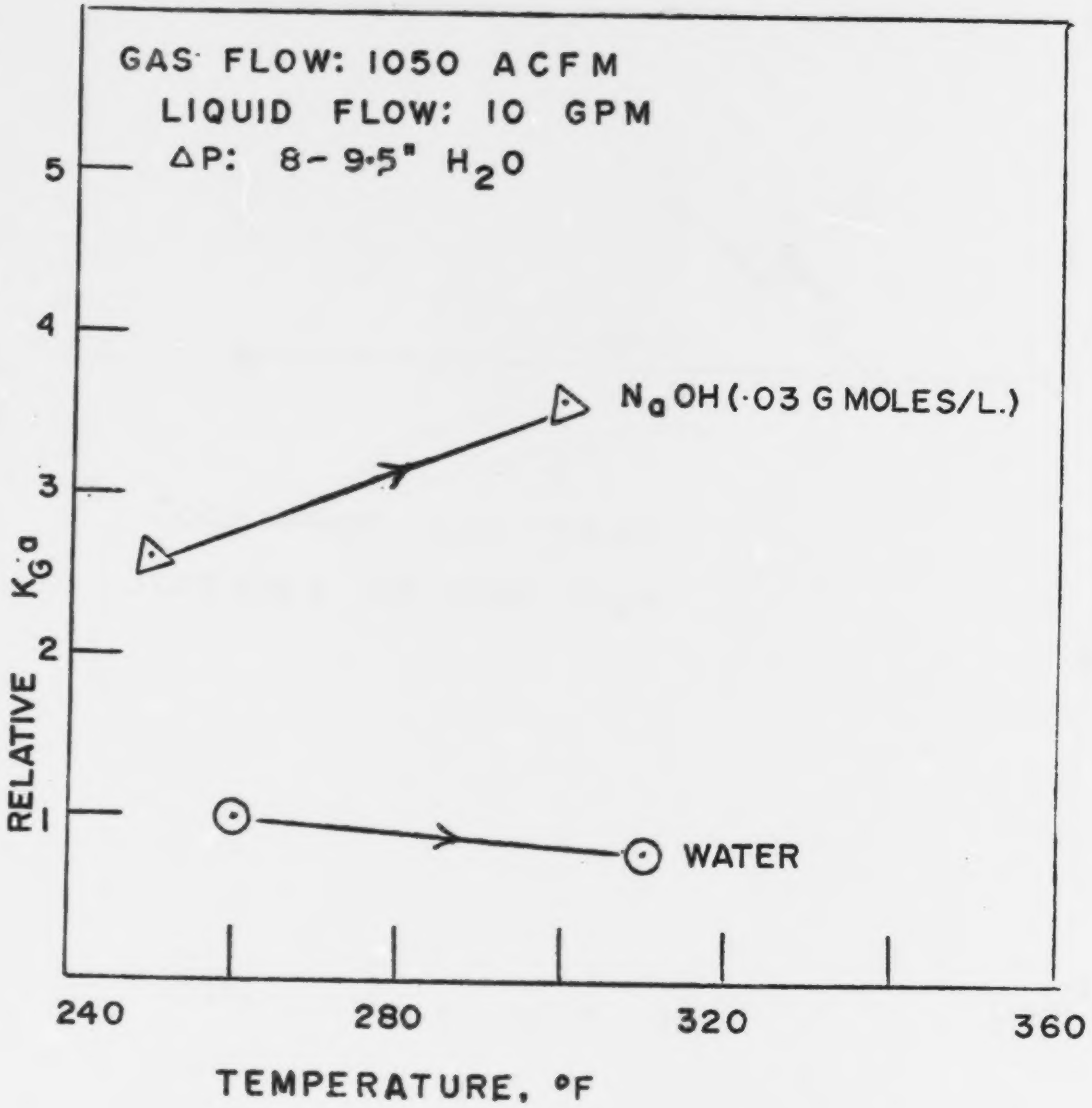


FIG. 6. EFFECT OF INLET GAS TEMPERATURE

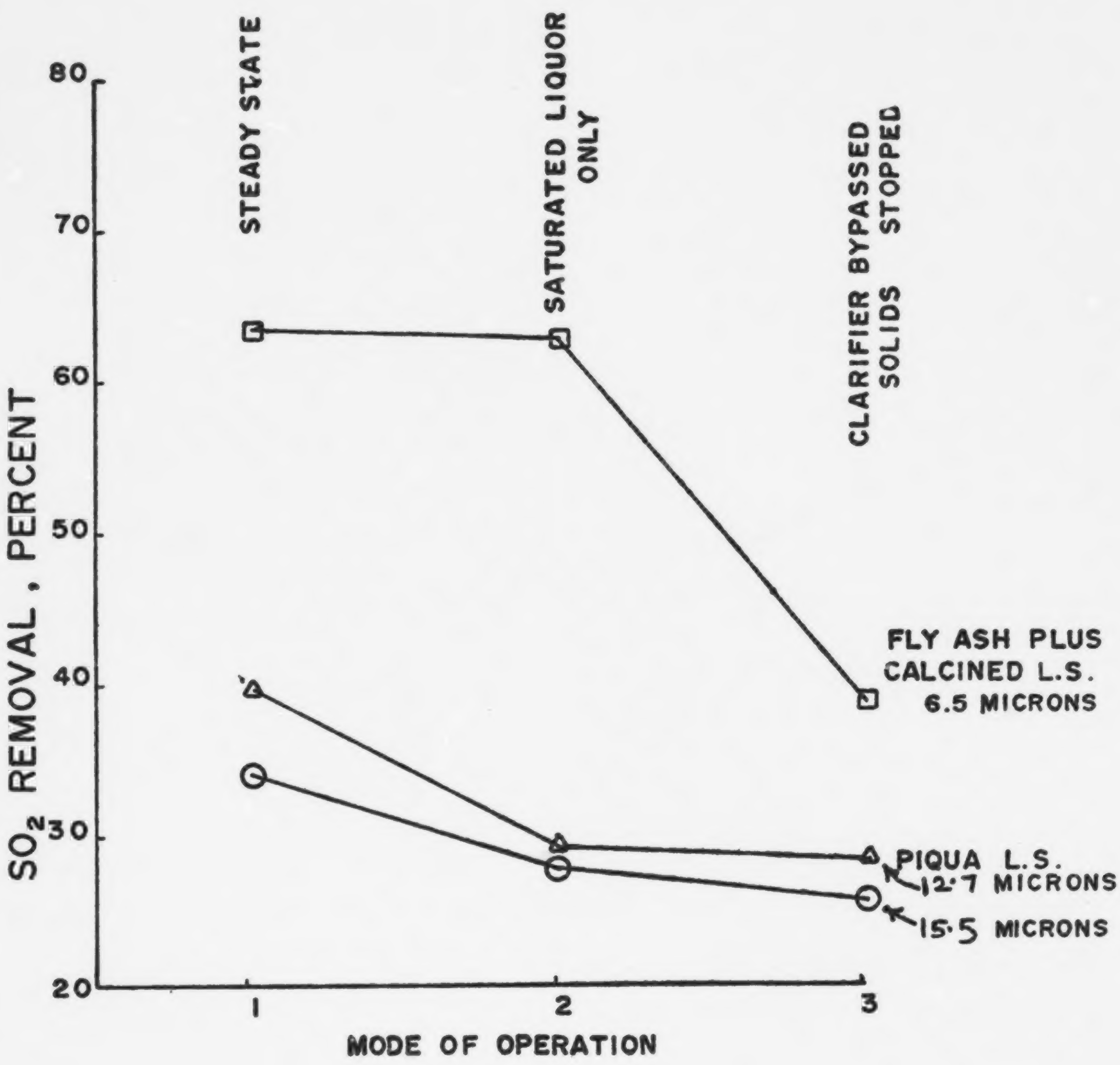


FIG.7 EFFECT OF LIMESTONE TYPE AND OPERATING CONDITIONS ON SULFUR DIOXIDE ABSORPTION

SO_2 REMOVAL USING CALCIUM BASED ALKALIES

PILOT PLANT EXPERIENCE

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SO_2 REMOVAL USING CALCIUM BASED ALKALIES

PILOT PLANT EXPERIENCE

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Introduction

Since January 1970, Chemical Construction Corporation in cooperation with various utility companies has undertaken extensive pilot plant work to obtain basic data for the design of commercial plants to remove sulfur dioxide from boiler flue gases using calcium based alkali namely limestone ($CaCO_3$), lime (CaO), Dolomitic limestone ($CaCO_3 \cdot MgCO_3$), Dolomitic lime ($CaO \cdot MgO$), and carbide sludge. In addition to obtaining basic design information, extensive useful information regarding scaling build up problems, effects of delay tank, particle size, and quality of limestone on SO_2 removal efficiency, were obtained.

In this presentation, we would like to present our experiences and important findings from the pilot plant work done to remove sulfur dioxide from boiler flue gases, usin calcium based alkali.

Pilot Plant Work

Chemical Construction Corporation, has conducted several pilot plant test programs for sulfur dioxide removal using calcium based alkali. Pilot Plants were installed a eight different power generating stations, all of whom use coal as the fuel. Of the total of eight, seven were balanced draft boilers, and one was a cyclone type boiler.

Pilot Plant Work (Cont'd)

Table I is the summary of boiler type, type of fuel and its sulfur and ash content, SO_2 and dust loadings in the flue gas, for the eight generating stations. A total of fourteen limestones, five different types of lime, one dolomitic limestone, one dolomitic lime, and one type of carbide sludge were tested. Table III summarizes the composition of limestones tested, Table IV summarizes the composition of various limes, and Table V summarizes the composition of dolomitic lime and limestone, and carbide sludge. Both 325 mesh and 200 mesh limestones were tested. Lime was always slaked in accordance with standard slaking procedure.

Pilot Plant Facility

A generalized pilot plant will include a two stage scrubber-absorber system, an I.D. Fan, recycle pumps, agitated delay tank, slaking system, lime or limestone slurry tank, a thickener, and a filter. Table II provides a summary of pilot plant equipment installed at various power plants, the type of alkali used, and the mesh size to which it was ground.

The flue gas from the generating unit was taken downstream of the Air heater. The duct size and location were determined to obtain an isokinetic sample while the boiler is operating at or near capacity, and the gas volume measured at the outlet of the scrubber system is 1500 cu. ft. / min (saturated). The scrubber-absorber system consisted of two W-A venturi scrubbers arranged in series.

Pilot Plant Operation

Flue gas, isokinetically withdrawn downstream of the air heater, enters the first stage scrubber, where SO_2 and fly ash are simultaneously removed by intimate contact with recycled slurry of $CaSO_3$, $CaSO_4$, $Ca(OH)_2$ or $CaCO_3$ and fly ash. The recycled slurry is introduced into the scrubber tangentially through open pipes, and it swirls down the converging section of the scrubber, thus completely wetting it. This liquor forms a curtan of liquor across the throat, and the accelerating gas shatters it into small droplets, which provide surface for dust collection and absorption of sulfur dioxide.

The cleaned flue gas and liquor enter the separator where liquor is separated by gravity, and any liquor carryover is separated by cyclonic action.

The flue gas now enters the second stage-venturi absorber-where SO_2 is absorbed by contacting with recycled slurry. The flue gas is then exhausted to atmosphere after passing through an I.D. Fan.

The make up limestone or lime slurry is added to the suction side of the second stage recycle pump, and the bleed from the second stage enters the suction side of the first stage recycle pump. The bleed from first stage is sent to thickener, the overflow

Pilot Plant Operation (Cont'd)

returning to the scrubber-absorber system. The thickener underflow is then filtered, the filterate returned to the system, and the cake is piled.

In the case where thickener and/or filter is not included, the bleed from first stage or thickener underflow is sent to sewer or ash pond for disposal. In case a delay tank is part of the pilot plant facility, the bleed from second stage, and first stage product liquor are sent to delay tank. The delay tank liquor is then recycled to the first stage scrubber.

Samples and Data

The flue gas samples were taken at the inlet of first and second stage, and outlet of second stage, and SO_2, NO_x and dust loadings were determined. Various liquor samples were taken and analyzed-both liquid and solid phases. Temperatures and pressures of various streams were measured.

Fly ash samples were collected and particle size determinations and mineral analysis were made. Lime and/or limestone samples were analyzed and analysis compared with suppliers' data. Coal samples were collected during pilot plant operation and proximate and ultimate analysis were performed. Table VI summarizes the analytical data collected during each pilot plant operation.

Boiler operating data, namely Air heater temp., excess oxygen, steam production, and

Samples and Data (Cont'd)

generating load, were also collected during the pilot plant operation.

SO_2 Removal Using Limestone

During the pilot plant work at various power plants, fourteen different limestones were tested. The composition of these limestones is presented in Table III. The $CaCO_3$ content ranged from a low of 86% to a high of 99.3%. The effects of various operating variables on SO_2 removal efficiency were determined. Table VII summarizes the various variables and their ranges studied.

Effect of Limestone Quality on SO_2 Absorption

The quality of limestone varies from mine to mine, and from region to region. Of the limestones tested, limestones 2 through 10 were from one geographical region, 12 through 14 were from another region, and 1 and 11 were from two other regions. Table VIII summarizes the data showing the effect of limestone quality on SO_2 absorption.

For limestones 2 through 5, limestone 4 was found to be the least reactive, when ground to 325 mesh, whereas limestone 4 was the most reactive when ground to 200 mesh.

For limestones 12, 13 and 14, the least reactive was 14 when ground to 325 mesh, whereas it was the most reactive when ground to 200 mesh.

Effect of Limestone Quality on SO_2 Absorption (Cont'd)

The SO_2 removal efficiency ranged from 30 to 80 percent, and of the 14 limestones tested, only two were found to be reactive enough to provide 70%+SO_2 removal efficiency at a reasonable stoichiometry. This is not adequate to meet present pollution codes for sulfur dioxide.

There is a wide variation in SO_2 removal efficiency with the variations in limestone quality. From the data obtained so far, it is still not possible to accurately predict SO_2 removal efficiency, just from the knowledge of the composition of the limestones.

Effect of Particle Size on SO_2 Abosrption

Smaller the particle size, larger the surface area available for absorption of SO_2. The surface area for 325 mesh particles is approximately 70% more than that for 200 mesh particles. This clearly shows that limestone ground to 325 mesh should provide higher SO_2 removal efficiency than that ground to 200 mesh. Table IX is a summary of data showing effect of particle size on SO_2 absorption. The data does prove that 325 mesh limestones are more reactive than 200 mesh limestones, except for limestone no. 14. The extra operating and investment cost to grind 325 mesh limestones must be compared with the cost for a higher stoichiometric requirement and/or for delay tank, to attain the same SO_2 removal efficiency.

Effect of Limestone Stoichiometry on SO_2 Absorption

The $CaCO_3$ reacts with SO_2 according to the following chemical reaction,

Effect of Limestone Stoichiometry on SO_2 Absorption (Cont'd)

$$CaCO_3 + SO_2 + 2H_2O \longrightarrow CaSO_3 \cdot 2H_2O + CO_2$$

One mole of $CaCO_3$ reacts with one mole of SO_2, to form a mole of Calcium Sulfite ($CaSO_3 \cdot 2H_2O$). Thus, a 100% stoichiometric limestone requirement means one mole of $CaCO_3$ for each mole of SO_2. The 150% stoichiometric requirement means 1. 5 mole of $CaCO_3$ for each mole of SO_2. Theoretically, higher the stoichiometry, higher the SO_2 absorption. Table X summarizes the data showing the effect of stoichiometry on absorption of SO_2. The data clearly shows that SO_2 absorption efficiency does increase with increase in stoichiometry. The increase in SO_2 absorption efficiency is not significant enough, compared with the increase in stoichiometry.

Effect of Delay Tank on SO_2 Absorption Efficiency

As a result of SO_2 absorption using limestone, calcium sulfite is formed. This calcium sulfite is presumed to form an inert coating on the limestone particle, thus making limestone unavailable for further reaction. The purpose of the delay tank is to remove this inert coating, and thus make more limestone available for absorption of SO_2. A delay tank has also been used in Howden - ICI process, to minimize and control scaling problems by holding the slurry leaving the scrubber for a period long enough for the supersaturation to dissipate on the surface of suspended crystals.

During the pilot plant work, a study was undertaken to determine the effectiveness of the delay tank in improving the SO_2 absorption efficiency. The delay tank was included either in the first stage recycle liquor loop, or second stage recycle liquor loop, or in

Effect of Delay Tank on SO_2 Absorption Efficiency (Cont'd)

both recycle liquor loops.

In the case of delay tank in the second recycle loop, the slurry leaving the scrubber, and make up limestone slurry were held in the delay tank. The liquor from the delay tank was sent to the scrubber for absorption of SO_2. The bleed from the second stage delay tank liquor, was sent to the suction side of first stage recycle liquor pump. In the case of a delay tank in the first stage recycle loop, the bleed from second stage, and the slurry leaving the scrubber, were held in the delay tank.

Table XI summarizes the data showing the effect of delay time on SO_2 removal efficiency increases with increase in delay time. In one case, the SO_2 removal efficiency increased by as much as 19 points, whereas in the other cases, the increase was about 12 points.

The recycle liquor pH increased with the increase in delay time. In one case, the pH increased from 4. 9 to 6. 5, and in the other cases it increased from 5. 2 to 5. 9.

The use of a delay tank was found to be more effective in the first stage recycle liquor loop, as any percentage point increase in SO_2 removal efficiency is a full point increase

Effect of Delay Tank on SO_2 Absorption Efficiency (Cont'd)

in efficiency, whereas in the case of a second stage loop, it is only a fraction of a point. The use of delay tank in both the recycle liquor loops did not produce any significant increase in SO_2 removal efficiency over the use of delay tank in the first stage recycle liquor loop.

Overall Summary - SO_2 Removal Using Limestone

The quality of limestone does have a marked influence on SO_2 removal efficiency, with increase in stoichiometry, use of a delay tank, use of 325 mesh ground limestone, and with a high quality limestone, SO_2 removal efficiency as high as 80-85% can be attained.

SO_2 Removal Using Dolomitic Limestone and Dolomitic Lime

The dolomitic limestone contains carbonates of both calcium and magnesium. The composition of the dolomatic limestone is presented in Table V. A maximum SO_2 removal efficiency of 30% was attained in a single stage venturi scrubber system. The pH values for the feed slurry were about 8.0 and for the recycle liquor between 4.8 and 5.5.

The composition of the dolomitic lime is given in Table V. With the use of dolomitic lime in a single stage scrubber system, the maximum SO_2 removal efficiency attainec was 92% (1800 ppm inlet) with 130% stoichiometric lime requirement. The presence of magnesium oxide make dolomitic lime much more reactive.

SO_2 Removal Using Dolomitic Limestone and Dolomitic Lime (Cont'd)

It is our opinion, that dolomitic lime or limestone should not be used as an absorbing reagent in the case of a throw away process, as the soluble magnesium-sulfur compounds will result in water pollution problems.

SO_2 Removal Using Lime

Five different types of limes have been evaluated to determine SO_2 removal efficiency. The compositions of these five limes are presented in Table IV. The summary of the data showing the effect of stoichiometry, the effects of single stage and two stage operations and effects of modified single and two stage operations on SO_2 removal efficiency, is presented in Table XII. The data clearly shows:

(a) That increasing the stoichiometry, increases the SO_2 removal efficiency.

(b) That with the use of a two stage scrubber system a better utilization of lime can be achieved. At 100% stoichiometry, the SO_2 removal efficiencies for a single stage and two stage operations are respectively 60% and 83%.

(c) That the modified single or two stage systems provide still better utilization of lime, as can be seen from the following:

	% Stoichiometry	%Efficiency
Single Stage	100	60.0
Modified Single Stage	100	72.0
Two Stage	100	83.0
Modified Two Stage	100	88.0

(d) That with the use of lime as an absorbing agent, adequate SO_2 removal efficiency can be attained to reduce outlet SO_2 concentrations less than 150 ppm.

SO_2 Removal Using Carbide Sludge

Carbide sludge is produced during the manufacture of acetylene using calcium carbide.

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

The composition of the carbide sludge tested in the pilot scale is presented in Table V. The data for the single and two stage operations, showing the effects of stoichiometry, effects of modified one and two stage operations and effects of delay tank are summarized in Table XIII. The data clearly shows:

(a) That increasing the stoichiometry, increases the SO_2 removal efficiency.

(b) That use of two stage operation provides higher SO_2 removal efficiency than single stage operation.

(c) That modified system provides improved performance.

(d) That use of delay tank further improves SO_2 removal efficiency, and

(e) That with the use of carbide sludge as an absorbing agent, adequate SO_2 removal efficiency can be attained to reduce outlet SO_2 concentrations below 150 ppm.

Thickener and Filter Tests

During every pilot plant operation, equipment vendors performed necessary tests to determine thickener and/or filter performance. This was essential so that the vendors can supply suitable equipment with guaranteed performance for the commercial plant.

Thickener underflow concentrations in the range of 40 - 60% solids can be attained

Pilot Plant Work (Cont'd)

with clean overflow. In some cases use of flocculants was found necessary. With the use of a suitable vacuum filter, filter cake containing 60% - 80% solids can be obtained. The cake characteristics were studied and were found suitable in most cases for truck transportation.

Open Loop vs. Closed Loop Operations

In the open loop operation, make up lime or limestone slurry was added to the scrubber system, and the bleed from the scrubber system was discharged to the disposal area. In the case of partially closed loop operation, the scrubber bleed was sent to a thickener, the thickener overflow was returned to scrubber and the underflow was sent to disposal. In the case of completely closed loop operation, the thickener underflow was sent to a filter, the filtrate was returned to the scrubber, and filtered cake was sent to disposal.

Essentially the same SO_2 removal efficiency was obtained during open and closed loo type operations. During closed loop operations, except for some scaling and build u no noticeable difference in operation was observed.

Scaling and Build-Up Problems

The use of lime or limestone slurry as the absorbing agent results in a scrubbing liquor containing calcium sulfate, calcium sulfite and unreacted calcium carbonate or calcium hydroxide. The recycle liquor being a slurry, the clear solution is always

Scaling and Build-Up Problems (Cont'd)

a saturated solution, containing $CaSO_3$, $CaSO_4$ and $CaCO_3$. The mechanism for SO_2 absorption and precipitation of sulfite or sulfate is believed to be as follows:

$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(l)}$$

$$CaCO_{3soln} + H_2SO_3 \rightarrow CaSO_{3soln} + H_2O + CO_2$$

$$CaSO_3 \text{ excess} \rightarrow CaSO_3 \text{ saturated} + CaSO_3 \text{ ppt.}$$

$$CaCO_3 \text{ solid} \rightarrow CaCO_{3soln}$$

Sulfur dioxide from the flue gas dissolves in water to form sulfurous acid, which reacts with calcium carbonate in solution to form calcium sulfite. This causes a super saturation in terms of calcium sulfite, resulting in precipitation of calcium sulfite. Some of the calcium carbonate from the solid phase dissolves in the solution thus causing it to reach saturation. Any oxidation of sulfite to sulfate causes sulfate to precipitate out. The inverse solubilities of both calcium sulfite and calcium sulfate, with increasing temperature, does enhence the precipitation of both compounds. This precipitation occurs within the scrubber on various surfaces, causing the scaling and build-up problems.

The basic scaling characteristics of solutions containing calcium sulfite and calcium sulfate, are inherent in nature. Scaling and build-up will occur, regardless of the type of scrubber-absorber selected, but how fast and how much will depend on type of scrubber and method of operation. The proper point of introduction of lime or limestone in the scrubber recycle liquor loop, the presence of delay tank, and selection of scrubbing equipment with minimum internals, should minimize scaling and buildup

Scaling and Build-Up Problems (Cont'd)

problems. Based on pilot plant work done, it is our opinion that scaling and buildup problems will be more pronounced during a closed loop operation than during partially open or open loop operations. We are of the opinion that if and whenever possible, the slurry of calcium - sulfur compounds should be kept outside the path of gas flow, to attain highest possible reliability for boiler operation, to generate electricity.

Summary

The limestone quality seems to vary from one region to another region, and has significant effect on SO_2 absorption. Smaller particle size and higher stoichimetry help increase SO_2 absorption efficiency. The presence of a delay tank increases efficiency or help reduce limestone requirements for the same efficiency. With a suitable combination of limestone quality, particle size, reasonable stoichiometry and delay time, SO_2 removal efficiency as high as 80-85% can be attained. With the use of lime or carbide sludge as the absorbing agent, one can attain 90+% efficiency at 130% or less stoichiometric lime requirement. Selection of alkali should be made after proper economic evaluation which should include stoichiometric requirement, alkali cost, grinding and preparation costs, disposal cost and installed equipment cost.

Scaling and build-up problems are inherent when using lime or limestone slurry as absorbing liquor. Proper methods of operation, and selection of scrubber-absorption equipment, may help reduce the frequency and extent of these problems.

Table I. Summary of Boiler Operating Data

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Boiler Type	Balanced Draft	Balanced Draft	Balanced Draft	Cyclone	Balanced Draft	Balanced Draft	Balanced Draft	Balanced Draft
Fuel	Coal	Coal	Coal	Coal	Coal	Coal	Coal	Coal
% Ash	22 - 23	20 - 25	20 - 25	20 - 25	16. 8-28. 9	16. 3-17. 8	9 - 11	10. 3 - 12. 4
% Sulfur	0. 68-0. 71	5. 5 - 7. 3	5. 5 - 7. 3	5. 5 - 7. 3	3. 2 - 5. 5	2. 1 - 2. 3	2. 5 - 2. 8	3. 3 - 4. 1
Inlet SO_2, ppm	450 - 575	4000-5200	4000-5200	4000-5200	1500-3800	1100-1600	1500-2200	1700-2250
Inlet Dust, Gr/SCFD	3. 9 -11. 7	4. 3 - 8. 3	4. 3 - 8. 3	0. 85 - 2. 5	4. 0 - 10. 0	3. 0 - 6. 0	3. 0 - 4. 5	3. 0 - 5. 0

Table II Summary of Pilot Plant Facility at Various Power Plants

Pilot Plant Facility	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
I. D. Fan	✓	✓	✓	✓	✓	✓	✓	✓
Single Stage	✓							✓
Two Stage		✓	✓	✓	✓	✓	✓	
Recycle Pumps	✓	✓	✓	✓	✓	✓	✓	✓
Delay Tank		✓	✓	✓	✓			
Thickener		✓		✓			✓	
Filter				✓			✓	
Closed Loop							✓	
Open Loop	✓	✓	✓	✓	✓	✓		✓
Slaking System	✓	✓				✓	✓	✓
Lime Slurry Tank	✓	✓			✓	✓	✓	✓
Limestone Slurry Tank	✓	✓	✓	✓	✓	✓		✓
Alkali Used								
Limestone	✓	✓	✓	✓	✓	✓		
Mesh Size								
-325	✓	✓	✓	✓	✓	✓		
-200	✓	✓	✓	✓	✓	✓		
Lime	✓	✓				✓	✓	
Dolomite								✓
Calcined Dolomite								✓
Carbide Sludge					✓			

TABLE III - SUMMARY OF LIMESTONE COMPOSITIONS

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
SiO_2		4.26	5.74	7.51	6.13	6.07	3.75	4.84	7.07	1.60	0.82			
Fe_2O_3		0.63	0.80	0.90	0.52	0.55	0.58	0.92	0.92	0.09	0.16			
Al_2O_3		0.36	0.53	0.60	0.61	0.48	0.24	0.38	0.44	0.28	0.18			
$CaCO_3$	95-98.25	91.84	88.98	85.78	91.67	91.72	94.22	88.56	86.71	96.81	95.21	99.3	86.8	93.4
$MgCO_3$		2.96	4.45	5.12	1.08	1.05	1.78	5.18	3.78	0.80	3.51			
R_2O_3							0.82	1.30	1.36		0.34			
S							0.068	0.07	0.06	0.06				
P	0.03-0.1													
Na-K oxides	0.2-0.22													
LOI		41.50	40.56	40.20	40.83	40.84	41.98	41.73	40.56	42.93				
Mesh-325		96	96	96	96	96	96	96	96	99+%		90+	90+	90+
-200		98	98	98	98	98	98	98	98			90+	90+	90+

TABLE IV - SUMMARY OF LIME COMPOSITIONS

	(1)	(2)	(3)	(4)	(5)
Cao	77.3	85.58	79.82	95.0	95.0
Mgo	0.2	0.52	0.23	1.08	1.08
Sio$_2$	21.5	0.77	1.09	1.3	1.3
Fe$_2$0$_3$	1.0	0.11	0.07	0.95	0.95
Al$_2$0$_3$		0.15	0.12		
R$_2$0$_3$		0.26	0.19		
S		0.014	0.01	0.03	0.03
L0I		12.75	18.95	1.75	1.75

TABLE V - COMPOSITIONS OF DOLOMATIC LIMESTONE & LIME & CARBIDE SLUDGE

Dolomatic Limestone		Dolomatic Lime	Carbide Sludge	
Cao	60	57	$Ca(OH)_2$	92.5
Mgo	40	43	$CaCO_3$	1.85
	97% thru	83% thru	Sio_2	1.50
	325 mesh	200 mesh	MgO	0.70
			R_2O_3	1.60

Chemical Construction Corporation

Pollution Control Division

Table VI Summary Of Analytical Data

Flue Gas

Dust loading, gr/SCFD
SO_2 loading, ppm
NO_x, ppm
Temp., °F
Pressure, " W. G.
at
1st stage inlet
2nd stage inlet
2nd stage outlet

Fly Ash

Particle size Distribution
Mineral Analysis
- P_2O_5
- SiO_2
- Fe_2O_3
- Al_2O_3
- TiO_2
- CaO
- MgO
- SO_3
- K_2O
- Na_2O

Coal

Ultimate Analysis
(as received & dry basis)
- Moisture
- Carbon
- Hydrogen
- Nitrogen
- Chlorine
- Sulfur
- Ash
- Oxygen

Proximate Analysis
(as received & dry basis)
- % Moisture
- % Ash
- % Volatile
- % Fixed Carbon
- BTU
- % Sulfur

Liquor Analysis

Slurry Analysis
- % Solids
- pH

Filtrate Analysis
- pH
- dissolved Solids
  - cl ppm
  - SO_4 ppm
  - Ca ppm
  - Mg ppm
  - SiO_2 ppm
  - SO2 ppm
- Phenol Alkalinity
- Total Alkalinity
- Conductivity mmhos

Dry Solids
- % SO_2
- % SO_4

Table VII Variables and Their Ranges

Variables	Range
Gas Veloctiy, ft/sec	50 - 250
Liquor to Gas Ratio, gallons/1000 ACFM	10 - 60
Limestone Stoichiometry	100 - 350
Limestone Mesh Size	200 mesh and 325 mesh
Delay Time, Minutes	10 - 60
Inlet SO_2 , ppm	450 - 5200

TABLE VIII - EFFECT OF LIMESTONE QUALITY ON SO_2 ABSORPTION

% $CaCo_3$	Limestone	Mesh Size	% Stoichiometry	Inlet SO_2 ppm	Efficiency
91.84	2	96% thru - 325 mesh	150	4150-4250	44.4
88.98	3				47.0
85.78	4				32.8
91.67	5				41.2
91.84	2	96% thru - 325 mesh	350	4050-4200	49.6
88.98	3				55.4
85.78	4				44.1
91.84	2	98% thru - 200 mesh	300	4400	39.4
88.98	3				37.2
85.78	4				44.7
99.3	12	90% thru - 325 mesh	150	1500	76.0
86.8	13				57.0
93.4	14				55.0
99.3	12	90% thru - 325 mesh	250	1500	80.0
86.8	13				70.0
93.4	14				60.0
99.3	12	90% thru - 200 mesh	150	1500	53.0
86.8	13				49.0
93.4	14				63.0
99.3	12	90% thru - 200 mesh	250	1500	65.0
86.8	13				56.0
93.4	14				68.0

Table IX. Effect Of Particle Size On SO_2 Absorption

Limestone	%$CaCO_3$	Mesh Size	Inlet SO_2, ppm	%Efficiency
12	99. 3	90%+ thru 325 90%+ thru 200	1500	75. 0 53. 0
13	86. 8	90%+ thru 325 90%+ thru 200	1500	57. 0 49. 0
14	93. 4	90%+ thru 325 90%+ thru 200	1500	55. 0 62. 0
11	95. 21	90%+ thru 325 90%+ thru 200	2900	62. 0 54. 0
2	91. 84	96% thru 325 98% thru 200	4000	44. 4 26. 1
3	88. 98	96% thru 325 98% thru 200	4200	47. 0 25. 4
4	85. 78	96% thru 325 98% thru 200	4200	32. 8 30. 5
5	91. 67	96% thru 325 98% thru 200	4200	41. 5 34. 0

TABLE X - EFFECT OF LIMESTONE STOICHIOMETRY ON SO_2 ABSORPTION

% $CaCo_3$	Limestone	% Stoichiometry	% SO_2 Efficiency
91.84	2-325 mesh	167	33.0
		321	45.0
91.84	2-200 mesh	162	27.0
		317	39.0
85.78	4-325 mesh	150	32.8
		329	49.4
85.78	4-200 mesh	132	30.5
		298	44.7
96.81	10-325 mesh	157	44.5
		232	54.5
		312	58.8
99.30	12-200 mesh	150	52.5
		200	61.0
		250	65.0
99.30	12-325 mesh	150	75.0
		200	78.0
		250	79.5
86.8	13-200 mesh	150	49.0
		200	56.5
		250	56.5
86.8	13-325 mesh	150	57.0
		200	61.5
		250	69.5
93.4	14-200 mesh	150	63.8
		200	64.0
		250	70.3
93.4	14-325 mesh	150	55.0
		200	59.0
		250	60.5
95.21	11-325 mesh	100	60.0
		150	64.0
		200	68.0

TABLE XI - Effect of Delay Tank on SO_2 Removal

Delay Tank in 1st Stage recycle liquor loop

Delay Time	% SO_2 Removal Efficiency	Recycle liquor pH	Limeston
T_1 = 0 min	46.0	4.9	3
T_2	58.5	5.4	
T_3	65.4	6.5	
T_1 = 0 min	64.0	5.2	11
T_2	74.0	5.6	
T_3	76.0	5.9	

Effect of Delay Tank location on SO_2 Removal Efficiency

Delay Tank Location	Delay Time	% SO_2 Removal Efficiency
1st stage	T_2	54.0
2nd stage	T_2	54.0
1st stage	T_3	65.0
2nd stage	T_3	64.0

TABLE XII - SO_2 Removal Using Lime

Lime	% Stoichiometry	Inlet SO_2 ppm	% Efficiency	
4	100	1500	83.0	Two Stage scrubber system
	140	1500	94.0	
	220	1500	95.0	
4	100	1500	88.0	Modified Two stage scrubber system
4	100	1500	60.0	Single stage scrubber system
	130	1500	64.0	
	145	1500	71.0	
	225	1500	77.0	
4	100	1500	72.0	Modified single stage scrubber system
	130	1500	88.0	
2	100	4000-6400	66.0	Single stage scrubber system
	130	4000-6400	75.0	
	150	4000-6400	80.0	
2	100	4000-6400	80.0	Two stage scrubber system
	140	4000-6400	89.0	

Table XIII SO_2 Removal Using Carbide Sludge

% Stoichiometry		Inlet SO_2 ppm	% Efficiency
100	Single Stage	2500 - 3000	62.0
100	Modified Single Stage	2500 - 3000	69.0
100	Modified Single Stage and Delay Tank	2500 - 3000	72.5
130	Single Stage	2500 - 3000	73
130	Modified Single Stage	2500 - 3000	78
130	Modified Single Stage and Delay Tank	2500 - 3000	79.5
100	Two Stage	2500 - 3000	74.0
100	Modified Two Stage	2500 - 3000	78.0
100	Modified Two Stage and Delay Tank	2500 - 3000	92.0
120	Two Stage	2500 - 3000	85.0
120	Modified Two Stage	2500 - 3000	92.0
120	Modified Two Stage and Delay Tank	2500 - 3000	93.0

A PILOT PLANT TEST PROGRAM FOR SULFUR DIOXIDE REMOVAL FROM BOILER FLUE GASES USING LIMESTONE AND HYDRATED LIME

AT

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ABSTRACT

A pilot plant test program to determine the performance and optimum operating conditions of a Chemico Venturi Scrubber System for the simultaneous removal of fly ash and sulfur dioxide was performed at Union Carbide Corporation's coal-fired power station near Marietta, Ohio.

Hydrated lime and limestone were evaluated for sulfur dioxide removal during the test program. Fly ash removal efficiency of the venturi scrubber was determined simultaneously with sulfur dioxide removal.

The test program was performed in three phases:

1. Fly ash scrubbing using water as the scrubbing media.
2. Sulfur dioxide absorption using a hydrated lime slurry.
3. Sulfur dioxide absorption using a limestone slurry.

This paper discusses the effect on sulfur dioxide absorption of such operating variables as liquid to gas ratio, stoichiometry, number of stages, and delay tank.

Based upon the results obtained from the pilot plant tests, it was concluded that satisfactory technical performance using limestone or hydrated lime in a two-stage venturi system could be achieved on a full-scale plant. Estimated capital and operating costs for a full-scale installation are presented.

INTRODUCTION

Many coal-burning power generating plants are being required to reduce particulate and sulfur dioxide emissions. Some approaches being taken to control the particulate emission problem are wet scrubbers, more efficient electrostatic precipitators and conversion to oil. To decrease sulfur dioxide emissions, either the use of low sulfur content fuels or various methods of desulfurizing the flue gases can be utilized. Each approach poses many technical and economic problems, and considerable effort is being expended to develop the most acceptable solutions.

At Union Carbide's Marietta, Ohio power station, a captive high ash and sulfur content coal has been burned since the start of operations in 1951. The station is equipped with mechanical collectors and two-field electrostatic precipitators to control particulate emissions.

The Parkersburg, West Virginia/Marietta, Ohio Interstate Abatement Conference issued specific recommendations in March and April, 1970, calling for a 70% reduction of sulfur oxide emissions and a decrease in fly ash emissions to a 0.14 lb./mm Btu heat input level. Compliance dates for these recommendations are April, 1972 for sulfur oxides and March, 1973 for particulate. Proposed State of Ohio regulations, now pending, are more stringent. Particulate emissions of 0.10 lb./mm Btu heat input and sulfur dioxide emissions of 1.6 lb./mm Btu heat input, equivalent to about a 1% sulfur coal (12,500 Btu/lb.), are proposed for this size plant.

A survey of possible methods of reducing emissions pointed out the desirability of evaluating the use of wet scrubbing, with a calcium compound throw-away system, for control of both the particulate and sulfur dioxide emissions. To evaluate such a system, a two-stage venturi scrubber pilot plant supplied by Chemical Construction Corporation was installed at the power station. Major aims of the program were to determine particulate removal capabilities of the venturi scrubber and the sulfur dioxide removal efficiencies of two alkaline materials--limestone and hydrated lime.

DESCRIPTION OF POWER STATION

The Union Carbide power station is a high-load factor station, rated at 200 megawatts, located on the Ohio River near Marietta, Ohio. This station supplies power to all units of Union Carbide's manufacturing complex in Marietta. In addition to power, the station also provides process steam to the complex. This additional requirement results in a coal consumption equivalent to that of a 250 megawatt station.

The power station has four identical boilers, each currently equipped with a cyclone-type mechanical collector and an electrostatic precipitator. At full capacity, the flue gas quantity from each boiler is approximately 280,000 ACFM at 320° F. entering the collectors.

The coal burned at the plant has been, until recently, Meigs #9 Seam from Noble County, Ohio, with a typical ash and sulfur content of about 20% and 5%, respectively. Tests were made with this coal, although currently higher quality blend coal is being used to comply with interim emission reductions recommended by the Interstate Abatement Conference.

OBJECTIVE OF TEST PROGRAM

The objective of the pilot plant test program was to confirm engineering design parameters and develop design data for a commercial installation. The key elements of the program were:

1. To correlate particulate and sulfur dioxide removal efficiencies with various scrubber operating conditions.
2. To establish a relationship between outlet dust loadings and pressure drop across the venturi throat.
3. To determine sulfur dioxide absorption efficiencies using limestone and hydrated lime, and to evaluate the effect of the following variables:

   Limestone

   (a) particle size - nominal 200 mesh by Down and 325 mesh by Down
   (b) stoichiometric feed rate
   (c) liquid to gas ratio
   (d) delay tank

   Hydrated Lime

   (a) single-stage versus two-stage scrubbing
   (b) stoichiometric feed rate
   (c) liquid to gas ratio
   (d) delay tank
4. To confirm the optimum design conditions using limestone and observe the degree of scaling or depositing when operating for an extended test period.

PILOT PLANT

A slip stream for the pilot plant was withdrawn after the air preheater and before the mechanical collectors. Location and size of the gas withdrawal duct were determined by traverses to assure that an isokinetic flue gas sample was taken for the pilot plant. The isokinetic condition corresponded to capacity operation of the boiler and 1500 cfm saturated gas flow from the pilot plant.

A flow sheet of the 1500 cfm two-stage pilot plant is shown in Figure 1. Figures 2 and 3 illustrate the installation.

The alkali feed, for a two-stage configuration, is fed to the second stage recycle loop with the second stage bleed going to the first stage recycle loop. This gives an alkali flow countercurrent to the flue gas producing the most efficient absorption system.

The delay tank is part of the first stage recycle loop. Its purpose is to allow for additional reaction time and increased utilization of the alkali by providing time for removal of reaction products that coat the unreacted alkali. During two-stage testing, the second stage bleed is also fed to the delay tank.

The main components of the pilot plant are two wet approach venturi scrubber-separator units. The flue gas is drawn into the scrubber at the top and the recycle liquid is fed through tangential nozzles. The liquid creates a curtain across the venturi throat and the accelerated flue gas breaks up the liquid into fine droplets which effectively interact with the fly ash and sulfur dioxide.

The flue gases are disengaged from the slurry, in both separator stages, by centrifugal and gravitational forces.

The recycle slurry is circulated by stainless steel pumps and all recycle piping is of stainless steel construction. Magnetic rotameters are used to measure the flow.

An induced draft fan is used to pull the stack gas through the system. It is of stainless steel construction and is capable of pulling 1800 cfm with a maximum pressure drop of 56 inches w.g.

The other accessory equipment consists of:

(a) Two feed tanks of 5000 and 7000 gallon capacity
(b) A delay tank of 4500 gallon capacity
(c) Feed pumps with 20 gpm capacity
(d) Feed rotameters
(e) Stainless steel orifice plate and manometer, located upstream of the fan, for flue gas flow measurement
(f) Delay tank pump identical to the recycle pumps
(g) Stack gas reheater

RESULTS

Fly Ash Scrubbing

Phase I of the test program was to determine particulate removal when scrubbing with water. The throat velocity and liquid to gas ratios were adjusted to vary the pressure drop across the throat over a wide pressure range. The particulate sampling procedures employed were the methods recommended by the Industrial Gas Cleaning Institute. The results were as follows:

(a) At inlet dust loadings ranging from 5.2 to 9.6 grains/SCFD and averaging 7-8 grains/SCFD, the outlet dust loadings ranged from about 0.08 to 0.02 grains/SCFD over the range of 1.5 to 18.5 inches w.g. pressure drop.

(b) Particulate sampling was continued during the sulfur dioxide absorption program. The results showed that the outlet dust loadings were comparable to those obtained when scrubbing with water. During the two-stage scrubbing test work, additional particulate removal occurred in the second stage.

Sulfur Dioxide Absorption with Hydrated Lime

Phase II of the test program was to determine the sulfur dioxide absorption capabilities of hydrated lime. The hydrated lime, a by-product of the generation of acetylene from calcium carbide, was obtained as a nominal 50% solids content sludge. This sludge, if used on a commercial basis, would be 90-95% calcium hydroxide on a dry basis. However, the sludge fed to the pilot plant was only 80-85% calcium hydroxide, with 5-10% being calcium carbonate.

The tests performed were to determine the optimum operating conditions to remove 70% and 90% of the inlet sulfur dioxide, which ranged during the program from 2000-3200 ppm sulfur dioxide on a dry basis. Both single-stage and two-stage tests were performed. The results of the single-stage tests were as follows:

(a) At stoichiometries ranging from 90% to 150%, based upon inlet sulfur dioxide concentration, absorption efficiency, or removal of sulfur dioxide, ranged from 60-80%.

(b) Use of a delay tank improved the absorption efficiency at the lower stoichiometries but had less effect at the higher hydrated lime feed rates.

(c) For the delay tank tests no improvements were obtained for residence times beyond 25 minutes.

(d) Increasing the liquid to gas ratio from 20 to 60 gpm/1000 ACFM, significantly improved the sulfur dioxide removal efficiency.

After completion of the single-stage tests, two-stage tests were performed. In general, the effects of the various operating parameters were similar to that of single-stage tests with all values of sulfur dioxide removal about 10-20% higher. Values above 90% were obtained.

The use of a delay tank was found more beneficial at the lower stoichiometries just as it was for single-stage operation. Higher reagent utilization was found to occur when the delay tank was used, and therefore, a commercial design would be significantly benefited by its use.

Sulfur Dioxide Absorption with Limestone

Phase III of the test program was to determine the absorption capabilities of an available limestone analyzing 95% $CaCO_3$ and 3.5% $MgCO_3$ with the remainder being mineral inerts. This limestone, from Carntown, Kentucky, is a material currently utilized in other operations at Marietta and is normally received by barge. Only two-stage tests were performed since past experience indicated that 70% sulfur dioxide removal could not be obtained in a single-stage unit.

The results of the limestone tests were as follows:

(a) Increasing the stoichiometric feed rate from 130% to 230% increased the removal efficiency about 10%.

(b) The effect of liquid to gas ratio on sulfur dioxide removal efficiency was significant. Increasing the liquid to gas ratio by 30% improved the sulfur dioxide removal efficiency by better than 5%.

(c) The gain in sulfur dioxide removal efficiency was about 10% higher when using 325 mesh limestone than when using 200 mesh limestone.

(d) The use of a delay tank increased sulfur dioxide removal by as much as 10%.

(e) Values in excess of 75% sulfur dioxide removal were obtained using a delay tank and 325 mesh limestone.

Extended Limestone Test

The final portion of the program was to operate the pilot plant continuously for three days using 325 mesh limestone. The system was run in an open loop configuration with no attempt made to recover the bleed stream liquid. The results of the tests were as follows:

(a) A removal efficiency of better than 70% for the optimum design conditions selected was confirmed.

(b) The unit operated smoothly and continuously during the entire test period. No changes in the venturi or separator pressure drops were observed.

(c) Inspection of the piping, rotameters, pumps and tanks showed that scale formation or depositing was insignificant.

SUMMARY OF RESULTS

The results of the test program for the Meigs Seam coal and the specific removal reagents are summarized below:

1. Fly ash levels down to 0.02 gr/SCFD were obtained. This value is well below the Interstate Abatement Conference Recommendations and the proposed State of Ohio Regulations.
2. A sulfur dioxide removal efficiency of 70%, the requirement of the Interstate Abatement Conference, was readily attainable with a single-stage scrubber using hvdrated lime or a two-stage unit using limestone.
3. A sulfur dioxide removal efficiency of 90%, which would exceed the proposed State of Ohio Regulations, was attained using hydrated lime in a two-stage scrubber system.
4. A continuously operated three-day test using limestone developed no scaling or depositing problems.

PROJECTED ECONOMICS OF FULL-SCALE PARTICULATE AND SULFUR DIOXIDE SCRUBBING SYSTEM

It was concluded from the pilot plant tests that satisfactory technical performance using limestone or hydrated lime in a two-stage venturi system could be achieved on a full-scale plant. Studies for the projected full-scale installation were based upon an individual scrubbing train for each boiler in order to assure maximum reliability and on-time performance. Predicted removal efficiencies for the full-scale system were 99% for particulate, 90% for sulfur dioxide with hydrated lime, and 70% for Carntown limestone at a system pressure drop of 20 inches w.g.

Design and engineering work by Chemical Construction Corporation under way since January, 1971 and updated for information obtained from the pilot plant program, yielded estimated costs for a complete installation utilizing a two-stage hydrated lime system as follows:

Capital Costs		
Initial Scrubbing System on One Boiler		$ 3,900,000
Settling Basin for Scrubber Effluent		900,000
Hydrated Lime Materials Handling System		800,000
	Subtotal	$ 5,600,000
Three Additional Scrubbing Systems		9,000,000
	Subtotal	$14,600,000
Development Costs		
First Scrubbing System		$ 1,500,000
Remaining Scrubbing Systems		1,500,000
	Subtotal	$ 3,000,000
Capital Plus Development Costs	Total	$17,600,000

Annual Operating Costs

One Scrubbing System		
Energy		$ 80,000
Maintenance		150,000
Absorbent (Hydrated Lime) for 90% Sulfur Dioxide Removal		250,000
	Total	$ 480,000
Four Scrubbing Systems	Total	$1,920,000

The preceding cost estimates included the following specific items for each scrubbing system:

1. Chemico integral venturi scrubbers-mist eliminator units, with each stage a separate vessel.
2. Delay tank.
3. Flue gas reheater using process steam.
4. Steam turbine-driven fan to supply system pressure drop.
5. Recycle of pond water to system.

The estimates include connection into an exhaust stack, but not the stack itself.

Absorbent Cost Comparison

The following table shows a material cost comparison of hydrated lime vs. limestone for a scrubbing system on one boiler burning 250,000 tons of 5% sulfur content coal per year.

Basis: Total Sulfur - 12,500 tons/year
Total SO_2 - 25,000 tons/year

70% Removal of Total SO_2 - 17,500 tons/year
90% Removal of Total SO_2 - 22,500 tons/year

70% Sulfur Dioxide Removal

	Tons Required	Cost/Ton, $	Total Cost $	Cost/Ton of Coal Burned, $	Cost/Pound of Sulfur Dioxide Absorbed, ¢
Hydrated Lime	58,000	3.40 (1)	197,200	0.79	0.56
(50% solids)	58,000	3.90 (2)	226,200	0.91	0.65
Limestone	53,360	4.10 (3)	218,776	0.88	0.63
	53,360	4.30 (4)	229,448	0.92	0.66
		90% Sulfur Dioxide Removal			
Hydrated Lime	70,900	3.40	241,060	0.96	0.53

Cost Assumptions:

(1) Hydrated Lime @ $1.00/ton
(2) Hydrated Lime @ $1.50/ton
(3) Limestone @ $1.70/ton and grinding @ $0.80/ton
(4) Limestone @ $1.70/ton and grinding @ $1.00/ton

At the most favorable material costs for 70% sulfur dioxide removal, hydrated lime has about a 10% lower cost advantage.

A salient feature of hydrated lime favoring its selection over limestone is that about 55% as much absorbent solids and 65% as much absorbent - sulfur dioxide reaction product solids are handled in the system. Less waste product storage capacity would be required.

ACTION TAKEN BY FERROALLOYS DIVISION OF UNION CARBIDE

Concurrent with the activity discussed in this presentation, changing business conditions indicated that a high quality (10% ash, 0.8% sulfur) captive coal supply could be made available for the Marietta power station. Utilization of this coal, together with precipitator upgrading, has been determined to be the minimum capital solution for reducing Marietta power station emissions to meet existing recommendations and proposed regulations.

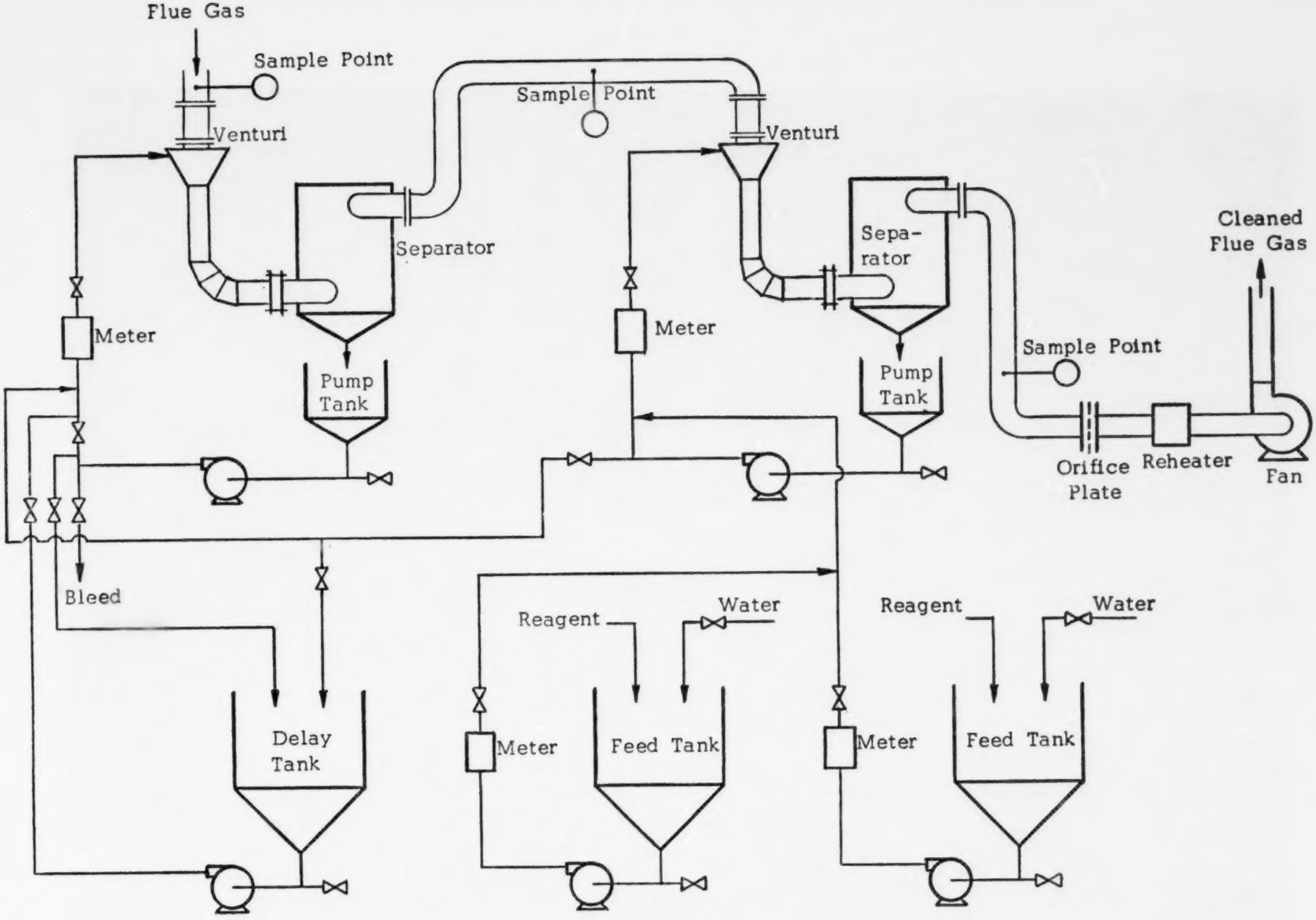

FIGURE 1
TWO-STAGE VENTURI SCRUBBER SYSTEM
SCHEMATIC FLOW SHEET

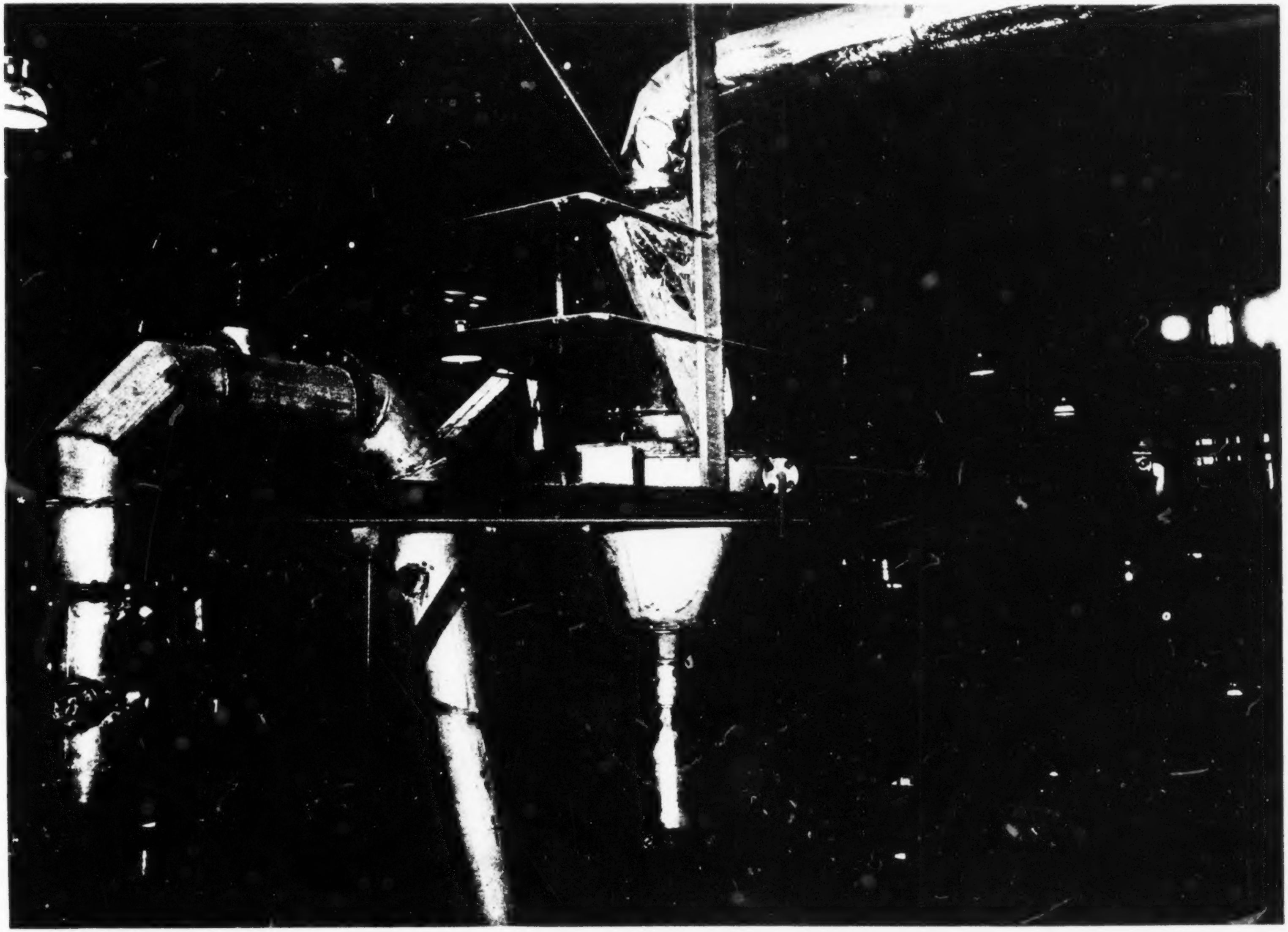

Figure 2

ENTRIES TO VENTURI SECTIONS - MARIETTA PILOT INSTALLATION

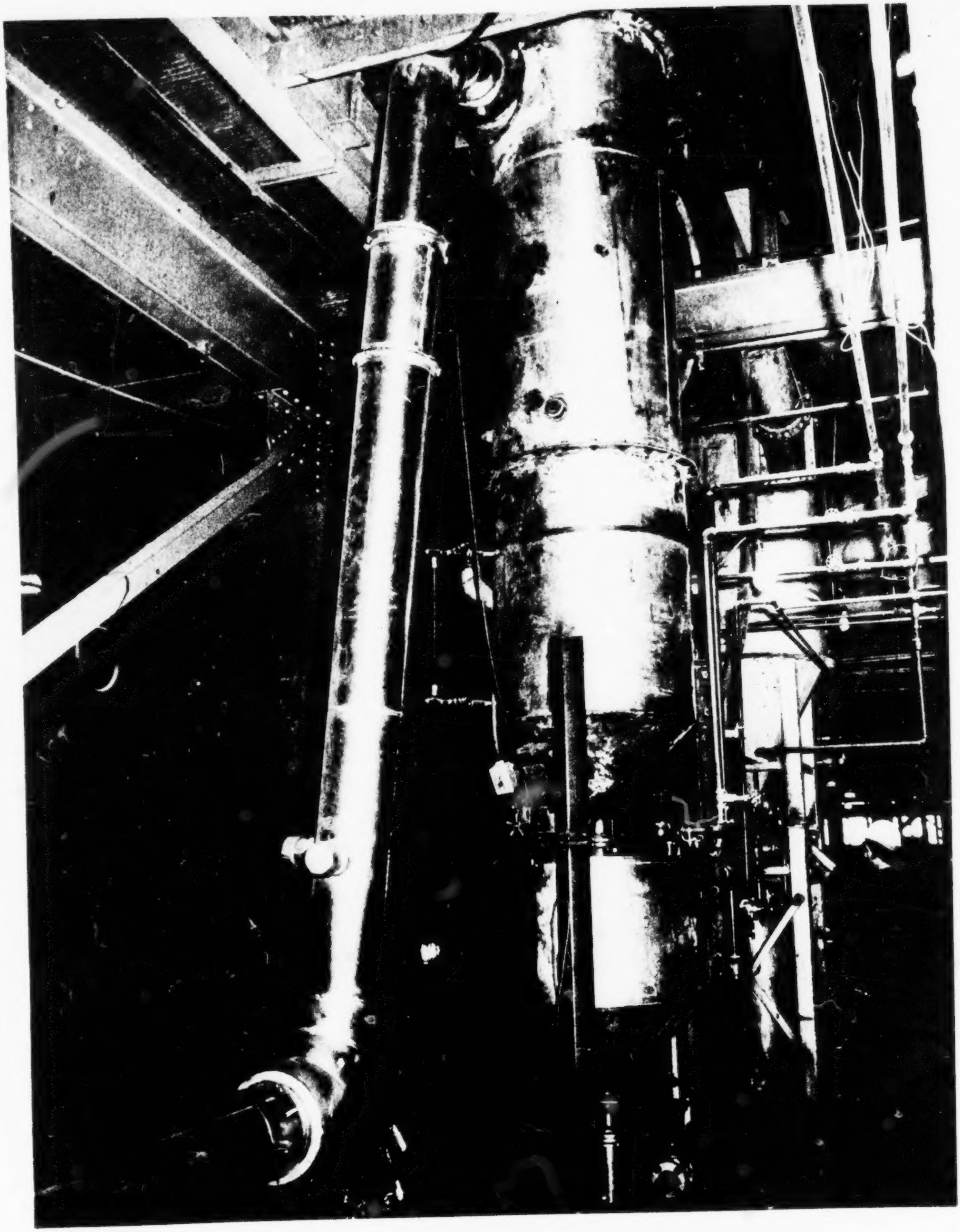

FIGURE 3

TWO-STAGE VENTURI SYSTEM - MARIETTA PILOT INSTALLATION

LIMESTONE SCRUBBING EFFICIENCY OF SULFUR DIOXIDE IN A WETTED FILM PACKED TOWER IN SERIES WITH A VENTURI SCRUBBER

By

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Prepared For:

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Lime/Limestone-Wet Scrubbing Symposium

New Orleans, Louisiana
November 8-12, 1971

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ACKNOWLEDGEMENTS

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Experiments were carried out at the Tidd Power Station of Ohio Power, a subsidiary of American Electric Power. The cooperation of AEP and the Tidd Power Station personnel played a key part in executing this study.

Part of the work reported here was conceived and performed by the Tennessee Valley Authority personnel. The progress resulting from the limestone tests is due, in part, to TVA participation.

LIMESTONE SCRUBBING EFFICIENCY OF SULFUR DIOXIDE IN A WETTED FILM PACKED TOWER IN SERIES WITH A VENTURI SCRUBBER

Sulfur dioxide removal from a power plant flue gas was studied in a 1,000 CFM pilot plant containing a packed tower and venturi scrubber combination. Absorption efficiencies were determined for a range of SO_2 concentrations in the gas-phase and limestone concentrations in the liquid slurry. Results of the absorption tests indicate removal efficiencies to be strongly affected by the inlet SO_2 concentration and the limestone stoichiometry. Reaction products deposition in the absorption tower were determined for various operating modes and/or conditions. Scaling of the tower absorber was controlled by maintaining a high liquid-to-gas ratio and high slurry concentration in the circulating liquor.

I. INTRODUCTION

Control of power plant sulfur dioxide emission has been under study at Research-Cottrell since the early 1960's. Initially, R-C investigators were concerned with the absorption characteristics of the Flooded Disc Scrubber (FDS), a venturi-type wet scrubber. Results of this experiment work demonstrated a low degree of SO_2 removal (40 to 60%) when lime was employed as a scrubbing agent. Scaling within the scrubber and auxiliary equipment was difficult to control during maximum absorption conditions. To achieve greater sulfur dioxide removal and controlled scaling, other conventional tower absorbers were screened. Bench-scale studies of select packing types showed that a particular wetted film packing with exceptionally low pressure drop characteristics and high specific surface was well suited for SO_2 scrubbing systems. In 1969, a 1,000 CFM pilot plant consisting of a FDS in series with a wetted-film packed tower was installed in Ohio Power's Tidd Plant. The results of earlier bench work and the status of the subsequent pilot plant program were reported in March, 1970 at the First International Symposium on Wet Limestone Scrubbing.[1,2]

Since the First Limestone-Wet Scrubbing Symposium, Cottrell Environmental Systems was contracted by EPA to execute a pilot plant study at the Tidd Power Station involving both lime and limestone. One objective of this program was the evaluation of the wetted-film packed tower absorption capabilities with limestone wet scrubbing.

The process conditions for the limestone tests were based upon bench scale studies performed by the Chemical

Development Division of the Tennessee Valley Authority, Muscle Shoals, Alabama. The absorption system simulated, to some respect, the Howden-ICI actual plant operation of the Fulham Power Station, London.[3]

Test results reported in this paper were previously presented at the 69th National Meeting of the American Institute of Chemical Engineers, Cincinnati, Ohio, May 16-19, 1971.

II. EQUIPMENT

A layout of the pilot plant system is given in Figure II-1. The absorption section of the pilot plant contained a Flooded Disc Scrubber (venturi scrubber) in series with a packed tower. The flue gas, containing both particulates and sulfur dioxide, passed first through the venturi where the entering gas quickly cooled to its dew point (≈120°F). Flue gas was removed isokinetically from the suction of the power station I.D. Fan.* Scrubbing solution or slurry entering the absorber tangentially above the throat flowed cocurrently through the venturi and into a cyclonic demister. The fly-ash-stripped gas then passed vertically through a conical hat gas/liquid splitter before entering the packed tower.

Slurry flow rates to the scrubber and other process units were measured by venturi-type flow meters. In-line pH probes were installed at the discharge of each scrubber. Also, immersion-type pH elements were placed in the clarifier and the hold tank.

The venturi scrubber is a cocurrent absorber with a variable throat orifice. Pressure drop across the scrubber can be varied by adjusting the disc position within a venturi throat, Figure II-2.

The packed tower is a countercurrent absorption device containing a packing with low pressure drop characteristics and high specific surface (68 sq.ft./cu.ft.). The packing, a rigid material fabricated from corrugated sheets of asbestos

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* Flue sampling contained particulate concentration of approximately 4.0 gr/scf from a pulverized coal combustion.

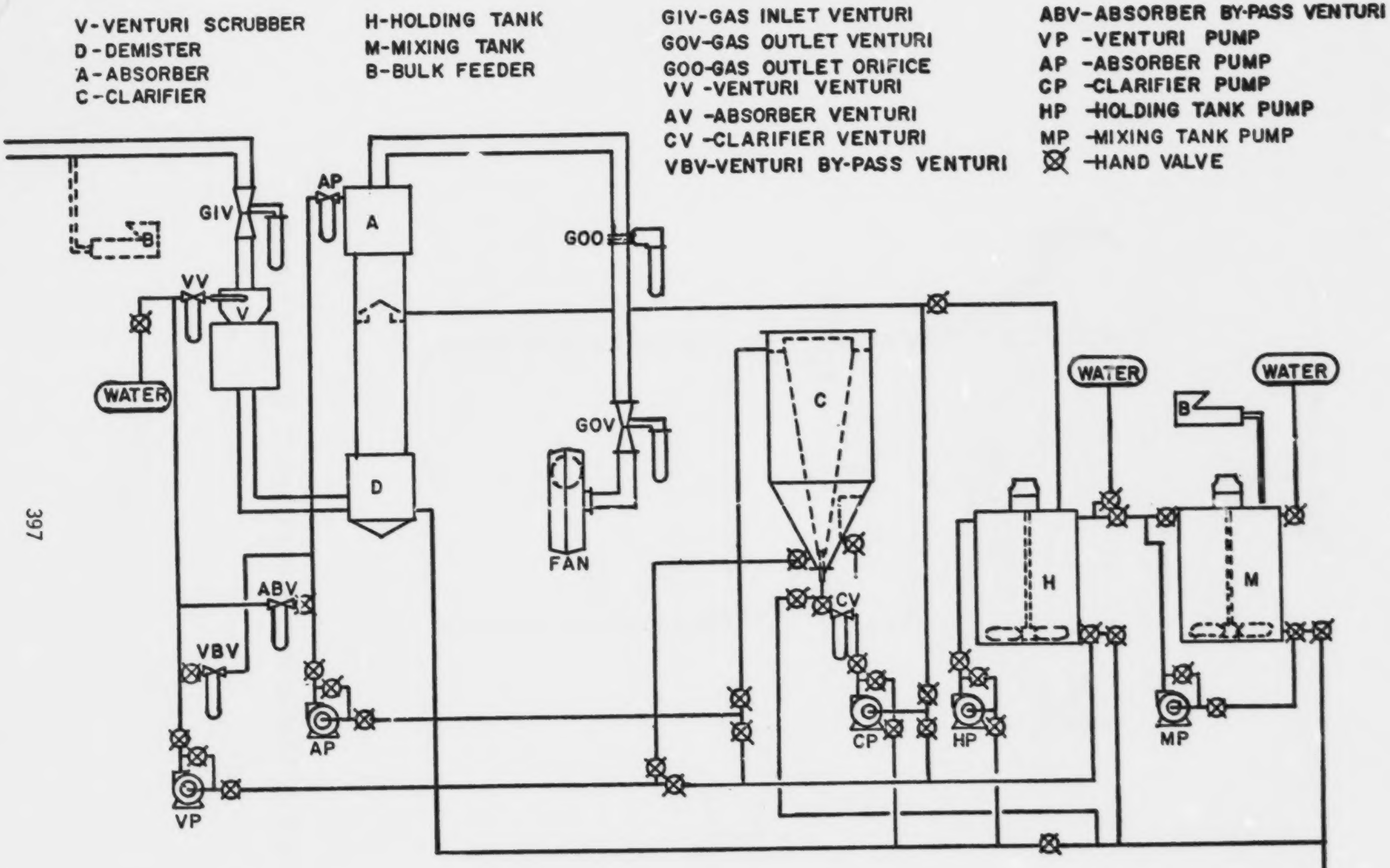


FIG. II-1 PILOT PLANT LAYOUT

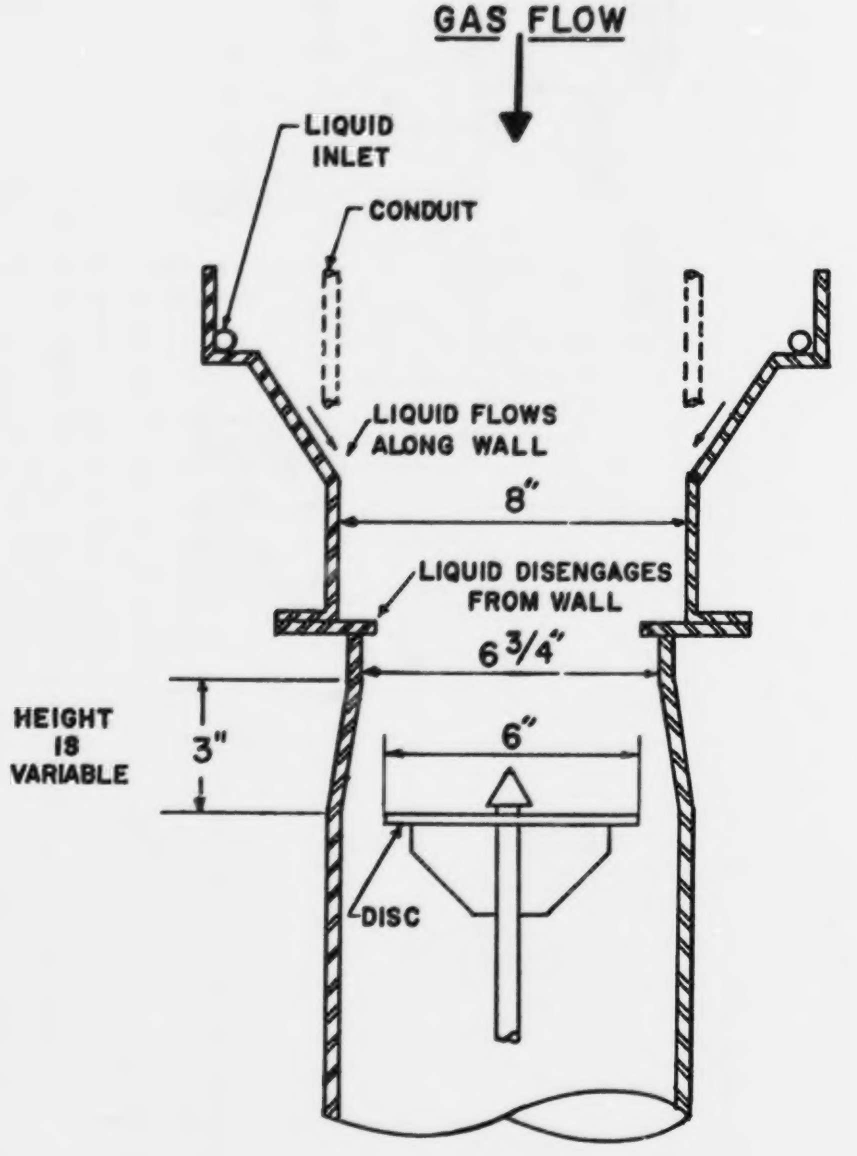


FIG. II-2 DIMENSIONS FOR FLOODED DISC SCRUBBER

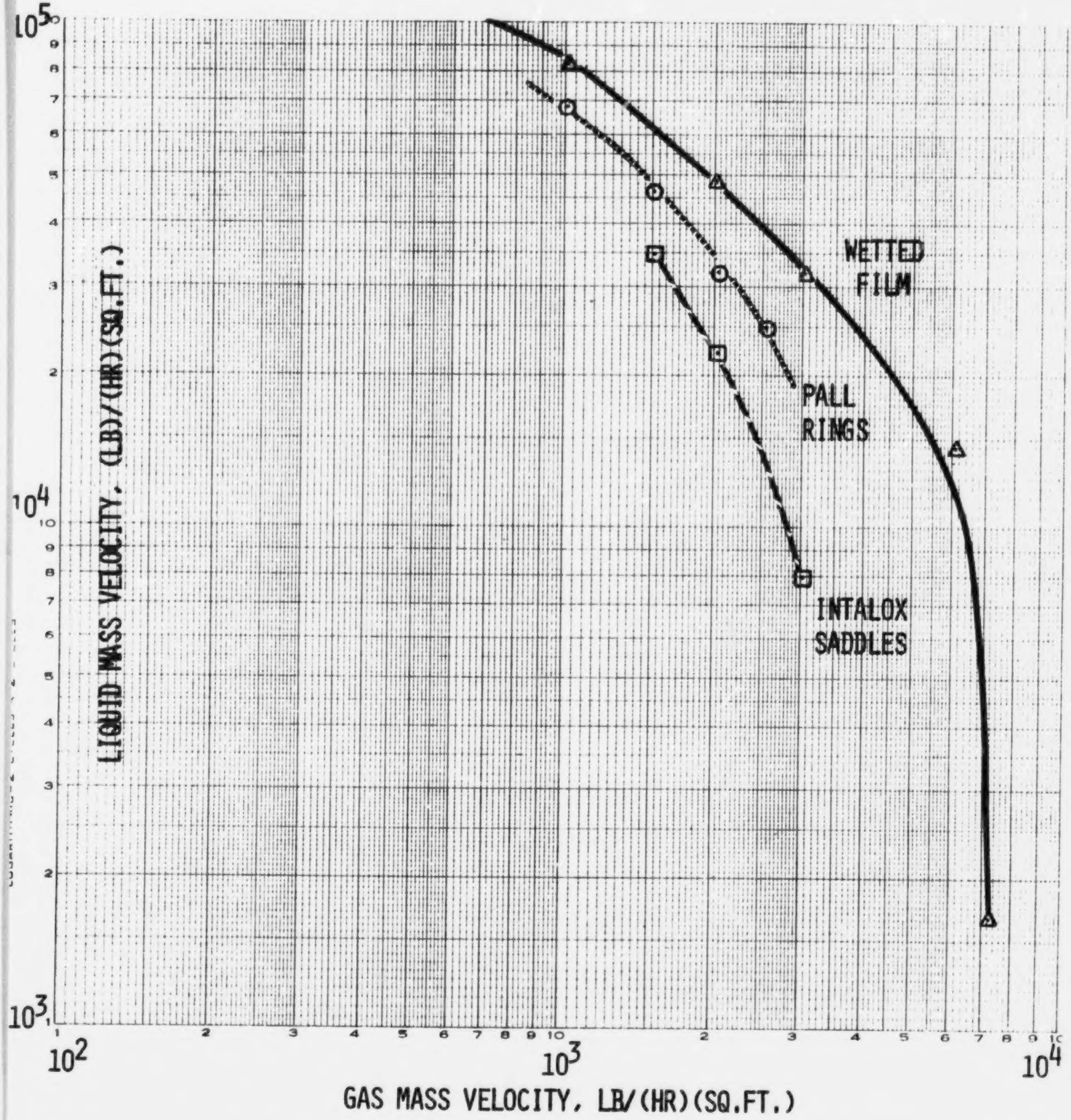
coated with neoprene, was five feet in height and sixteen inches in diameter. Pressure drop across the packing at gas velocities between 8 and 10 feet per second is approximately one inch of water with well-irrigated conditions.

Flooding characteristics of this packing were approximated by using the Eckerts flooding line correlation and a packing factor of 12.0.[4] The calculated flooding profile of the wetted film packing are compared to other high capacity packing in Figure II-3. As illustrated graphically, the wetted-film packing allows significantly greater liquid rates than either 3 inch plastic Pall rings or 3½ inch Intalox saddles.

PROCESS EQUIPMENT

Process Units	Size	Material Of Construction
FDS Scrubber	6" to 8" diameter See Figure 2.	316 SS
Packed Tower	16" diameter x 5'	316 SS
Tower Slurry Tank	1,500 gallons agitated	CS
Mixing Tank	1,500 gallons agitated	CS
Venturi Slurry Tank	55 gallons	CS
Cyclonic Demister	4' diameter x 4'	SS
Clarifier	1,200 gallons	CS
Blower	1,000 cfm at $\Delta p = 40$ inches H_2O	CS

CALCULATED FLOODING MASS VELOCITIES FOR THE WETTED-FILM AND OTHER HIGH CAPACITY PACKING



III. RESULTS

The limestone programs were carried out in two separate test series: several types of limestone were first processed in an open-loop system and absorption efficiencies were compared for each alkali type. In the second program, scale accumulation within the tower absorber was investigated using a limestone selected from the first test result. For the scaling runs, a closed-loop operating mode was used to minimize the process makeup water.

A. EFFICIENCY TESTS - OPEN-LOOP

Calcium carbonate materials (chalk, cement kiln dust, and two limestone grinds) were processed under similar operating conditions. Chalk (89%-200 mesh) and finely ground limestone (89%-325 mesh) allowed approximately the same absorption i.e. 96% removal. Limestone ground to 75%-200 mesh gave an efficiency between 81 to 88% while the cement dust showed the poorest results with 73% absorption. A chemical analysis for each of these materials is given in Table III-1.

Process modes selected for the pilot tests utilized the packed tower as the main contacting device. The venturi scrubber removed fly ash and a small portion of the inlet SO_2 by operating at a moderate pressure drop (6 to 7 inches of water). Fresh limestone slurry was fed first to the tower circulating tank where the bulk of the absorption took place. For maximum calcium carbonate utilization, the reaction products and the residual limestone were bled from the tower slurry tank and passed through a venturi circulation tank. The input limestone and the bleed were balanced so that a constant calcium concentration remained in the tower hold tank.

TABLE III-1

CALCIUM CARBONATE MATERIALS RECEIVED FROM TVA

Type	Particle Size	Amount Received lbs.	CaO	MgO	K_2O	Na_2O	Ign. Loss
Tiftona Limestone	75%-200M	4700	50.5	1.5	0.4	0.3	41.5
Tiftona Limestone	89%-325M	350	50.5	1.5	0.4	0.3	41.4
Cement Kiln Dust	90%-200M	1000	41.5	2.4	3.1	0.19	22.8
Selma Chalk	89%-200M	1000	43.1	0.59	0.49	0.18	35.1

Block diagrams illustrating the operating modes are shown in Figure III-1. A limestone slurry containing 2% by weight calcium carbonate was pumped to the Tower Slurry Tank from the Mixing Tank at a flow equivalent to the SO_2 stoichiometry desired.

For six of the seven efficiency tests, the stoichiometric input was between 100 and 110%.* One run was performed at 160% of the equivalent SO_2 to determine crudely the limestone stoichiometry effects. The sulfur dioxide concentration to the FDS was between 1,135 and 1,980 ppm. Although no particulate measurements were made, the normal fly-ash loading was from 3 to 4 grains per SCF.

The tower gas velocity for these tests was between 9.3 and 10.7 ft/sec. Liquid flows for most of the tests were maintained at 40 gallons per 1000 cu.ft.. A single test operated at L/G = 20 gallons per 1000 cu.ft.. Pressure drop on the tower was around 1.0 inches of water for most tests. Tests with chalk and cement were operated at slightly higher tower pressure differentials.

Operating results for these experiments are given in Table III-2. Each efficiency measurement listed is an average of four readings over a three-hour period. Liquid-to-gas ratio in the tower had considerable influence on SO_2 reduction. At L/G of 40 gallons per 1000 cf and a coarse grind limestone, the efficiency across the tower was 81.6%; however, at L/G of 20 for the same operating mode, the SO_2 removal dropped to 58.2%.

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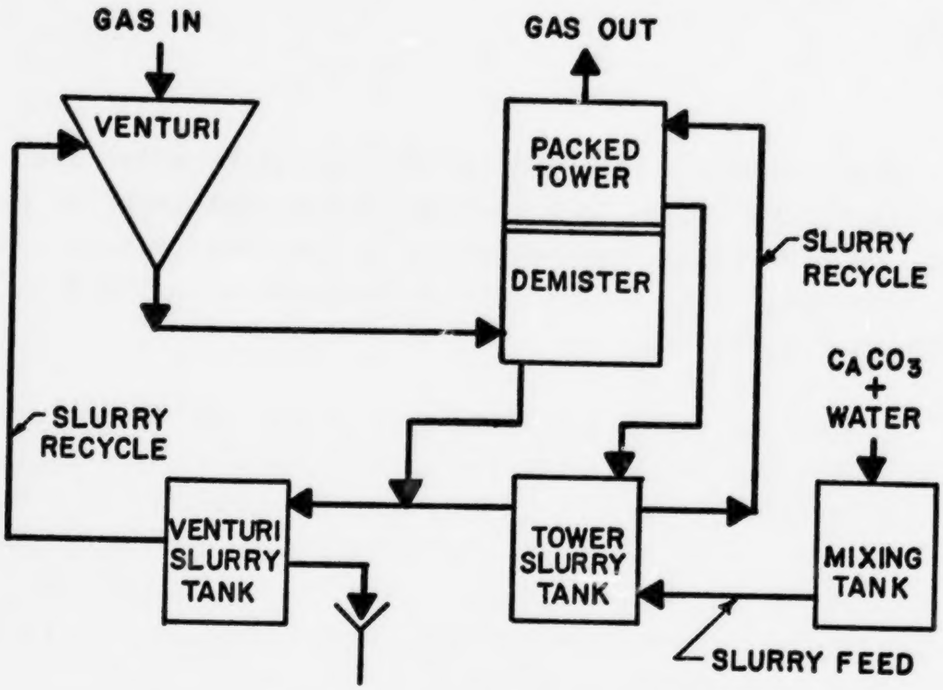
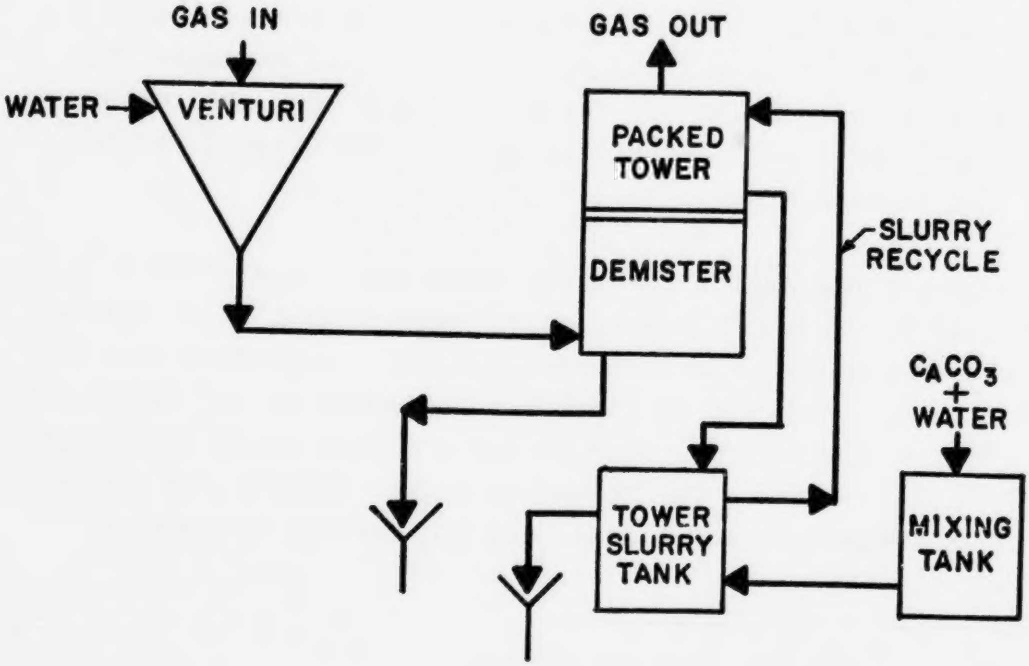
* Based on total SO_2 feed to system.



COUNTER-CURRENT SLURRY FLOW



WATER FEED TO FDS

FIG. III-1 OPERATING MODES USED FOR LIMESTONE EFFICIENCY TESTS

TABLE III-2

SUMMARY DATA SHEET FOR THE OPEN-LOOP EFFICIENCY TESTS[1]

Material Used	Selma Chalk	Cement Dust	Limestone				
			Fine	Coarse	Coarse	Coarse	Coarse
Test No.	A2	A3	A4	A5	A6	A7	A8
Tower Liquid Rate, GPM	35	36	24	24	32	18	32
FDS Liquid Rate, GPM	9.4	9	6	6	8	9	8
Gas Velocity, Tower, Ft/Sec.	10.7	10.7	9.3	9.3	9.6	10.7	9.6
Gas Velocity, FDS, Ft/Sec.	99	105	132	132	121	98	87
Tower Pressure Drop, inches H_2O	3.9	6.5	1.1	0.9	1.2	1.3	1.3
FDS Pressure Drop, inches H_2O	12.7	6.4	7.3	7.3	7.1	7.9	9.4
CaO/SO_2 Ratio	1.11	1.06	1.16	1.00	1.00	1.10	1.62
SO_2 Concentrations, PPM							
FDS in	1550	1135	1650	1980	1467	1637	1485
FDS out	1405	1025	1288	1795	1155	1415	1402
Tower out	48	268	62	209	212	592	199
Fraction of SO_2 Removed, %							
FDS	9.4	9.7	21.9	9.4	21.2[2]	13.6[2]	5.6
Tower	96.6	73.5	95.1	88.4	81.6	58.2	85.8
Overall	96.9	76.4	96.1	89.5	85.5	63.8	86.6
Gas Temperature, °F							
FDS in	371	377	361	361	348	391	369
FDS out	122	122	118	116	92	102	101
Tower out	114	116	110	109	91	99	98
Liquid Temperature, °F							
FDS in	119	121	118	116	40	40	41
FDS out	126	124	125	124	75	97	95
Tower in	112	114	110	110	89	95	96
Tower out	122	122	117	116	124	106	101
L/G ratio, FDS, Gal. per 1000 cf	10.4	10	10	10	10	10	10
L/G ratio, Tower, Gal. per 1000 cf	39	40	40	40	40	20	40

1. Operating conditions for each task shown are an average of four readings measured over a three hour period.

2. Water was fed to the FDS for this test.

B. SCALING EXPERIMENTS

During the limestone efficiency tests, some scaling did occur in the packed tower after the chalk, cement dust, and limestone were used as sorbate. Limestone alone did not show appreciable scale accumulation after 40 hours of contact. To determine definitively the scaling characteristics of the limestone/SO_2 absorption, a second test program was undertaken.

The operating conditions for minimum scaling were studied in four continuous 40-hour tests. Process parameters such as liquid-to-gas ratio, tower slurry tank residence time, and tower slurry tank temperature were varied. Scale deposition was measured by weighing the packing before and after each run. In most cases, new packing was installed for the subsequent test. Following these four preliminary experiments, an 80-hour continuous operation was executed and the scale accumulation measured. The closed-loop mode for the major portion of this test series is shown in Figure III-2.

1. Scaling

The conditions for each run are summarized in Table A-1 of Appendix A. Although some operational difficulties were encountered, and several process parameters were not consistent throughout any run, a general trend in scale accumulation could be seen. With high tower liquid-to-gas ratio, lower solids buildup was measured than with low L/G. Residence time for the slurry in the tower hold tank showed no effect as the hold time was varied from 30 to 10 minutes.

Profile of solids buildup on the packing going from the top to the bottom section did show a pattern of scale. Very little scale deposited in the top section while a consistent

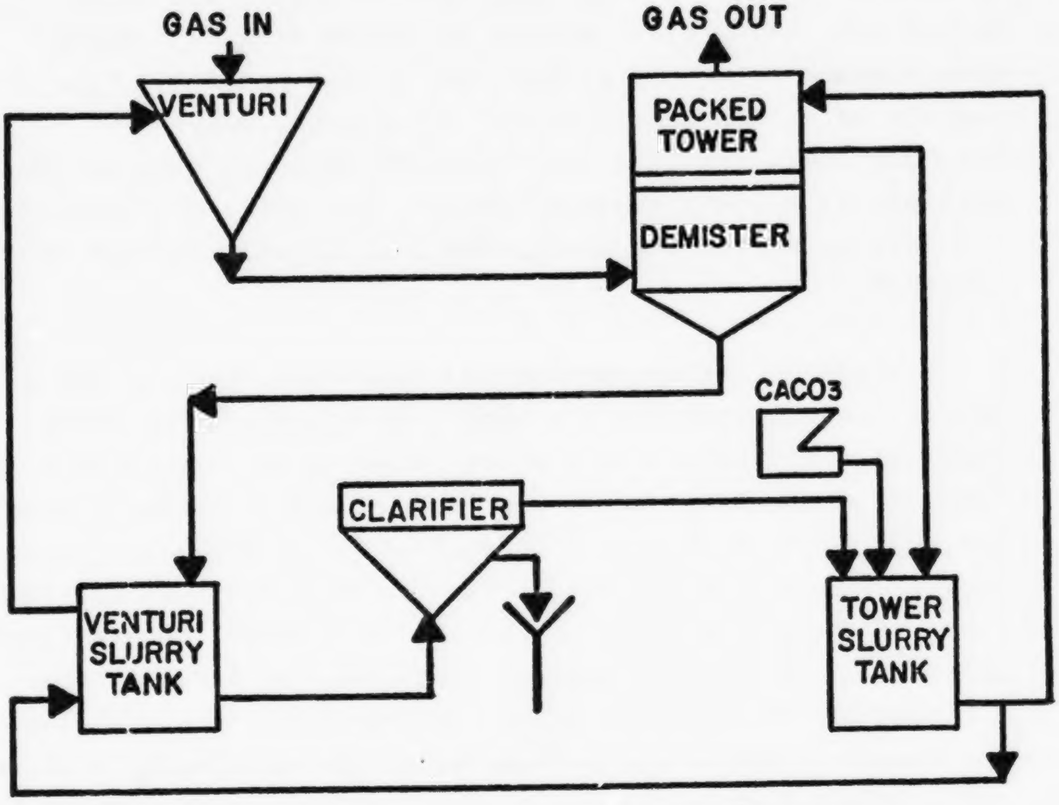


FIG. III-2 TWO STAGE CALCIUM CARBONATE SCRUBBER

quantity precipitated in the bottom four elements. This profile of solids buildup suggested an absorption supersaturation taking place within the tower with an induced encrustation after one or two feet in the packing. From the profile of solids deposited and the reduced deposition at high L/G, one could conclude that incoming solution from the hold tank was at a lower supersaturation, but once supersaturation did develop within the tower, the rate of encrustation was constant.

Based on the aforementioned reasoning, the operating conditions selected for the long-term demonstration tests combined a low level tower slurry tank volume with a high tower liquid-to-gas ratio, i.e. a ten minute residence time in the hold tank and a L/G of 40 gallons per 1,000 cubic feet. Stoichiometry at the start of the run was near 100% for the first 40 hours and 120% for the last 40 hours. Two limestone grinds were used throughout the run; for the first 40 hours, a limestone having 75%-200 mesh was employed, while during the second 40 hours the same material having 61%-200 mesh was fed. Solids concentration in the slurry was held between 4.4 and 8.9%. Chemical and particle analysis for these limestone materials are given in Table III-3.

2. Absorption

The absorption efficiency varied from a low of 55% to a high of 98%. Near the end of the run, the absorption was higher. A profile plot of the stoichiometry, slurry concentration, and tower efficiency is shown in Figure III-3.

During the continuous scaling run, a blower motor failure interrupted the test half way through the experiment. The

TABLE III-3

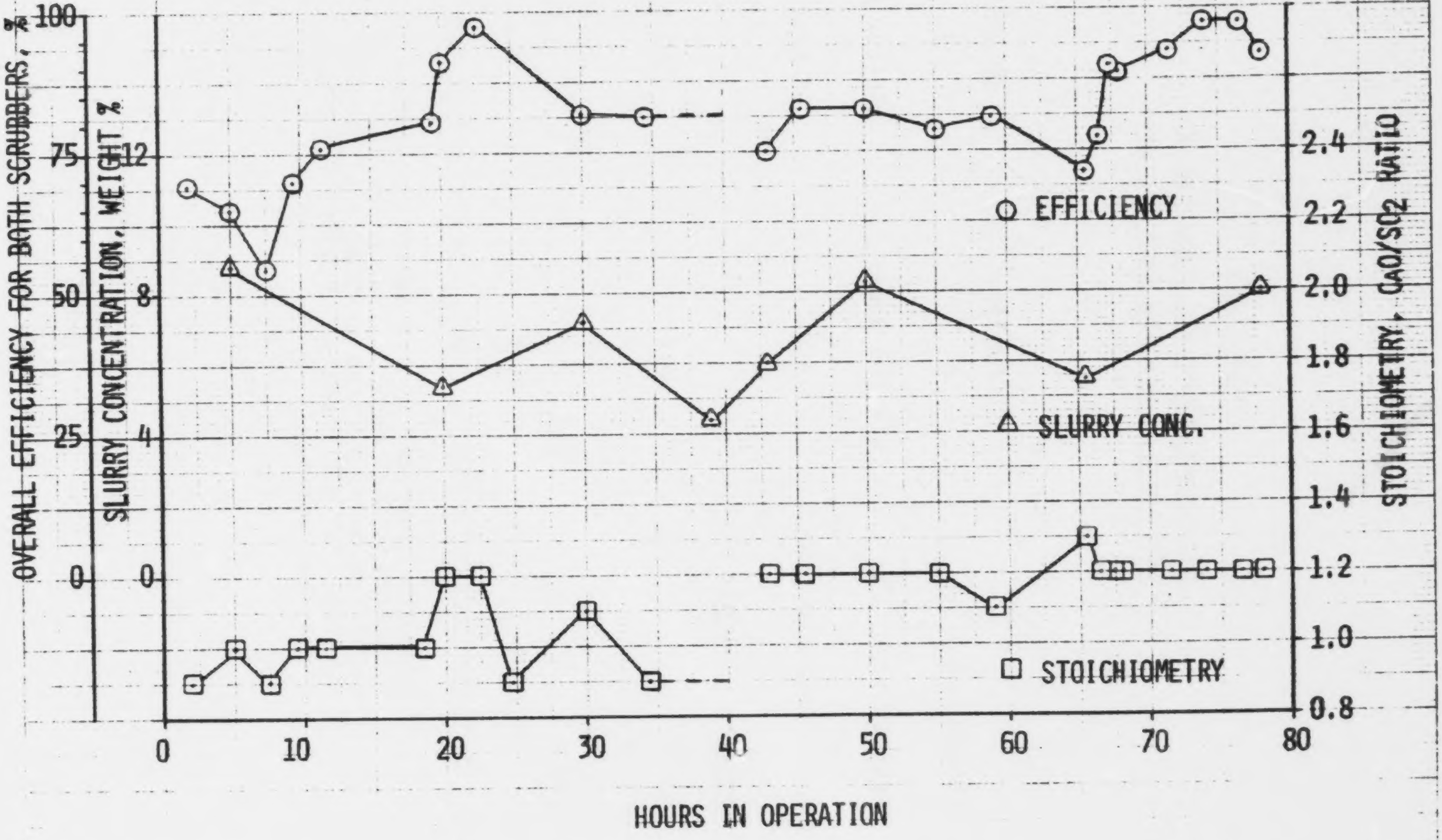
Limestone Materials Supplied By TVA For The Scaling Test Series*

Designation	Shipment A	Shipment B
Particle Size	61%-200 Mesh	75%-200 Mesh
Amount Received, lbs.	2000	4700
Chemical Analysis		
CaO %	50.8	50.5
MgO %	--	1.5
K_2O %	--	0.4
Na_2O %	--	0.3
Ign. Loss	41.5	41.5

* Limestone supplied by TVA called "Tiftona Limestone". Shipment "A" was a special supply of $CaCO_3$ for the scaling test series; Material "B" was received from TVA for the first test series.

FIGURE III-3

TASK C-6 EFFICIENCY PROFILE. SLURRY CONCENTRATION AND STOICHIOMETRY DURING THE RUN. SEE TABLE AI



packing was removed from the tower and each section was examined and weighed. Most of the encrustation deposited during the 40 hours was on the packing periphery. The encrustation had a mud-like consistency, not the hard scale observed with hydrated lime systems. Scale was not evident on the well-irrigated surfaces. For the second 40 hours, the same packing was used; encrustation that did develop was again predominantly at the periphery. Measured weight gain after 40 and 80 hours is given in Table III-4.

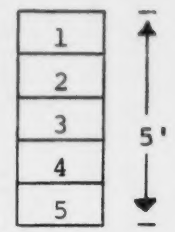
Within the first 40 hours, 10.5 pounds of solids had built up and during the next 40 hours an additional 12.5 pounds were deposited, weight gain determined on dried basis. No pressure increase could be measured throughout the 80-hour test. The amount of solids clinging to the packing was a small fraction of the packing void volume. Pressure measurements on the tower were approximately 1 inch of water at the start and finish of the tests, as given in Table A-1 in Appendix A.

TABLE III-4

Measured Scaling Accumulation On The Packing

Test Number	C-2	C-3	C-4 *	C-5 **	C-6 **	
Tower L/G gals/1000 cf	30	40-60	40	40	45	
Residence Time For Slurry	30	30	10	10	10	
Run Time, hrs.	40	40	40	40	40	80
Packing Number						
1 weight gain, lbs.	7	2	4	2	.5	3
2 weight gain, lbs.	14	9	13	5	1.5	3
3 weight gain, lbs.	13	10	15	8	1.5	7
4 weight gain, lbs.	16	10	14	8	3.5	6
5 weight gain, lbs.	14	12	20	8	3.5	4
TOTAL:	64	43	66	31	10.5	23

Packing Position



* Temperature on the tower circulating slurry not controlled at the inlet gas dew point. Heat losses on the slurry--10 to 15°F.

** Packing was weighed slightly wet.

IV. DISCUSSION

A. LIMESTONE EFFICIENCY TESTS - OPEN-LOOP

The venturi scrubber removed only a small fraction of the inlet SO_2 with each type of limestone. Between 6 to 22% of the SO_2 was sorbed for an inlet stoichiometry from 1 to 1.6, a liquid-to-gas ratio of 10 gallons per 1,000 cu.ft., and a pressure drop across the throat of 6.5 to 12.7 in. of H_2O. Such low scrubbing efficiency would not be practical for commercial application.

The packed tower performed outstandingly good with the limestone and chalk. The finely ground limestone (89%-325 mesh) removed nearly 95% of the tower inlet SO_2 (1288 ppm). Chalk with a through 200 mesh fraction of 89% absorbed 97% of the SO_2 at 1405 ppm inlet. Presumably, the high surface area characteristics of the chalk improved the absorption considerably. Cement kiln dust absorption of SO_2 was the lowest for the three limestone types tested. Although the cement dusts mesh size was very close to the chalk (90%-200 mesh) only 73% of the inlet SO_2 was removed. The cement dust may have been "dead burned" by the calcination conditions in the cement kiln, hence an appreciable portion could have been slow dissolving.

Liquid-to-gas ratio in the tower had a dramatic affect on the SO_2 efficiency. For a L/G of 40 gallons per 1,000 cubic feet and an inlet SO_2 at 1402 ppm, the SO_2 absorption was 85.8% while at L/G of 20 and an inlet SO_2 of 1415 ppm, the removal dropped to 58.2%. Such sensitivity to liquid flow implies a significant liquid-phase absorption resistance.

The flow rates through the tower at the liquid-to-gas ratio of 40 gals/1000 cf were well below the calculated flooding conditions indicated in Figure II-3. For example, at a L/G = 40 and a gas velocity of 9.6 ft/sec (Test No. A8 of Table III-2), the liquid and gas rates were 11,700(lbs)/(hr)(sq.ft.) and 2,160(lbs)/(hr)(sq.ft.), respectively. These values fall well below the flood condition. In fact, the liquid rate could have been doubled to 23,400(lbs)/(hr)(sq.ft.) or an L/G = 80 and still remain below 70% of the flooding liquid rate.

B. SCALING EXPERIMENTS

1. Scaling

The experimental technique used in measuring the scale accumulation on the packing was designed to qualitatively indicate the operating conditions affecting the deposition. Chemical composition and physical properties of the solid deposits were not analyzed. As previously mentioned, solids that did precipitate on the packing surface had a mud-like consistency, not the hard encrustation normally observed with lime.

Because of the packing design, a small diameter tower such as the pilot unit has a significant fraction of surface area that is not well-irrigated. When the corrugated sheets are cut in circular shapes, several peripheral layers are not exposed to the main irrigated pattern. It is in this peripheral region that much of the solids accumulated.

The scaling experiments, Tests C2 to C5, were originally designed to screen several tower process variables, i.e. liquid-to-gas ratio and tower slurry tank residence time. Tower slurry concentration and limestone stoichiometry were planned at 5% by weight and 100 to 110%, respectively. However, throughout the preliminary tests these variables were poorly controlled. Slurry concentration for tests C2 to C5 fluctuated considerably in some cases and stoichiometry was sporadic because of poor limestone feed control. No quantitative conclusions could be made with the measured scaling for the 40-hour tests, C2 to C5. Yet, two general trends could be seen: 1) the high liquid-to-gas ratio showed lower scaling, and 2) residence time in the tower slurry tank did not affect the solids accumulation. The operation and problems experienced in tests C2 and C5 were either eliminated or closely scrutinized during the final continuous test.

For the 80-hour run, solids buildup on the packing was reduced considerably as shown in Table III-4. The 40-hour preliminary experiment showed 30 to 66 pounds of solids accumulation in the five feet of packing while the final 80 hour run had 23 pounds. More important, however, the deposition that did occur was not a hard encrustation but a soft sludge precipitate and a considerable portion of this sludge collected on the packing periphery.

2. Absorption Efficiencies

The absorption efficiency for the preliminary scaling runs varied considerably because of the fluxuations in limestone stoichiometry, slurry concentration, inlet gas composition, and liquid-to-gas ratio. To avoid process variations in the long-term run, a strict control of the operation was maintained for the planned 80-hour tests. However, even with close scrutiny of these process variables, the absorption efficiency fluxuated considerably. To explain the efficiency variation, the operating conditions for the 80-hour run were examined carefully. Slurry chemical analysis performed by TVA and Radian Corporation were combined with the absorption efficiency, inlet SO_2 concentration, and slurry concentrations measured in the field.[5,6]

As a first step in the data analysis, the calcium carbonate concentrations were determined for the absorbate over the entire 80-hour run by digital computer simulation of the absorption process. With a known $CaCO_3$ analysis as a starting point, the $CaCO_3$ slurry concentration was calculated for each point in time that an efficiency measurement was made. The predicted carbonate slurry concentration fit well with the chemical analyses. The computer simulation did not take into consideration process changes such as spills, leaks, or uncontrolled water addition. A comparison of the computed and analyzed carbonate concentration is given in Table IV-1.

TABLE IV-1

LIMESTONE CONCENTRATION IN THE HOLD TANK DURING TASK C6

		Calcium Carbonate Concentration, %		
Date	Time	Computer Predicted	TVA	Radian
1/25	2230	1.89(Start)	1.89	--
1/26	1300	1.19	0.54	--
1/26	1500	1.19	--	1.13
1/26	2100	1.46	0.94	--
1/29	1400	0.36(Start)	0.36	--
1/29	2100	1.44	2.16	--
1/30	1230	1.32	1.65	--
1/30	0103	1.78	1.60	--

Using the computer-estimated value of limestone concentration, the analyzed sulfur dioxide absorption efficiency in the tower, and the measured tower hold tank slurry concentration, a linear correlation was developed which predicts the absorption efficiency for each of the limestone materials employed.

For the first 40 hours, where limestone ground to 75% -200 mesh was used, an outstandingly good correlation was realized. The absorption efficiency, predicted to within ± 1.9%, showed sensitivity to inlet SO_2 concentration and limestone concentration as seen below:

$$Y = 165.05 - 0.0463(\text{ppm}) + 30.48(\%\ CaCO_3) - 9.126(SL) \qquad (IV\text{-}1)$$

where Y = SO_2 absorption efficiency, %,
ppm = tower inlet SO_2 concentration in ppm,
% $CaCO_3$ = concentration of limestone slurry in the hold tank, %,
SL = concentration of all solid in hold tank, %.

Statistical parameters and the variable range for this correlation are listed in Table IV-2.

For the second half of the run, a similar linear correlation having a precision of ± 3% efficiency was developed for limestone with 61%-200 mesh. Here the last 26 hours of operation were studied so that a mixture of the two limestone types could be avoided. The predicted efficiency showed less

TABLE IV-2

STATISTICAL PARAMETERS FOR EFFICIENCY CORRELATION

(First 40 Hours Run*)

Number of Data Points = 30

Correlation Coefficient = 0.987

Standard Error For Estimate = 1.9

Significance of Regression (F) = 349

% Efficiency Range, Y = 53% to 97%

Sulfur Dioxide Inlet Range = 1160 to 1900 ppm

% $CaCO_3$ Range = 1.131% to 1.89%

% Total Solids Range, SL = 5.4% to 9%

---

* Limestone Used - Tiftona Limestone 50.5% CaO, 75% - 200 Mesh.

sensitivity to inlet SO_2 concentration and greater sensitivity to the limestone concentration, i.e.

$$Y = 56.273 - 0.0178(\text{ppm}) + 50.313(\%\ CaCO_3) - 4.15(SL) \tag{IV-2}$$

See Table IV-3 for statistical limitations.

To make use of these efficiency correlations, the limestone slurry concentrations must be known. Three factors influence the residual limestone concentration in the tower slurry liquor: 1) the actual absorption efficiency for the process, 2) the stoichiometric feed ratio of $CaCO_3/SO_2$, and 3) the overall slurry concentration. For a system with 6% total slurry, the limestone concentration can be predicted by:

$$\%\ CaCO_3 = 1.23 - 0.033(\%\ Y) + 2.236\ R \tag{IV-3}$$

where R = stoichiometric feed ratio, moles of $CaCO_3$/moles of SO_2.

Table IV-4 presents the condition for equation (IV-3).

Using this expression and equation (IV-1) or (IV-2), the absorption efficiency can be predicted for either limestone material for a liquid-to-gas ratio of 45 gallons per 1,000 cf., and a total slurry of 6% by weight.

Clearly, if absorption efficiency is dependent upon the limestone slurry concentration and the inlet SO_2 concentration, then one or both of these conditions must be controlled for a desired SO_2 removal. To illustrate this point, equations (IV-1) and (IV-3) were combined and the resulting relationship was plotted in Figure IV-1.

TABLE IV-3

STATISTICAL PARAMETERS FOR EFFICIENCY CORRELATION

(Last 26 Hours Run*)

Number of Data Points	=	26
Correlation Coefficient	=	0.95
Standard Error For Estimate	=	3.08
Significance of Regression (F)	=	69
% Efficiency Range, Y	=	75.5% to 97.9%
Sulfur Dioxide Inlet Range	=	960 to 1380 ppm.
% $CaCO_3$ Range	=	1.317% to 1.847%
% Total Solids Range, SL	=	5.5% to 8%

---

* Limestone Used - Tiftona Limestone 50.8% CaO, 61% - 200 Mesh.

TABLE IV-4

STATISTICAL PARAMETERS FOR STEADY STATE WT.% LIMESTONE CORRELATION

Number of Data Points = 16

Correlation Coefficient = 0.995

Standard Error For Estimate = 0.054

Significance of Regression (F) = 741.8

% $CaCO_3$ Range = 0.1616% to 2.07%

% Efficiency Range, Y = 53% to 92%

Range For Stoichiometric Ratio = 1.0 to 1.3

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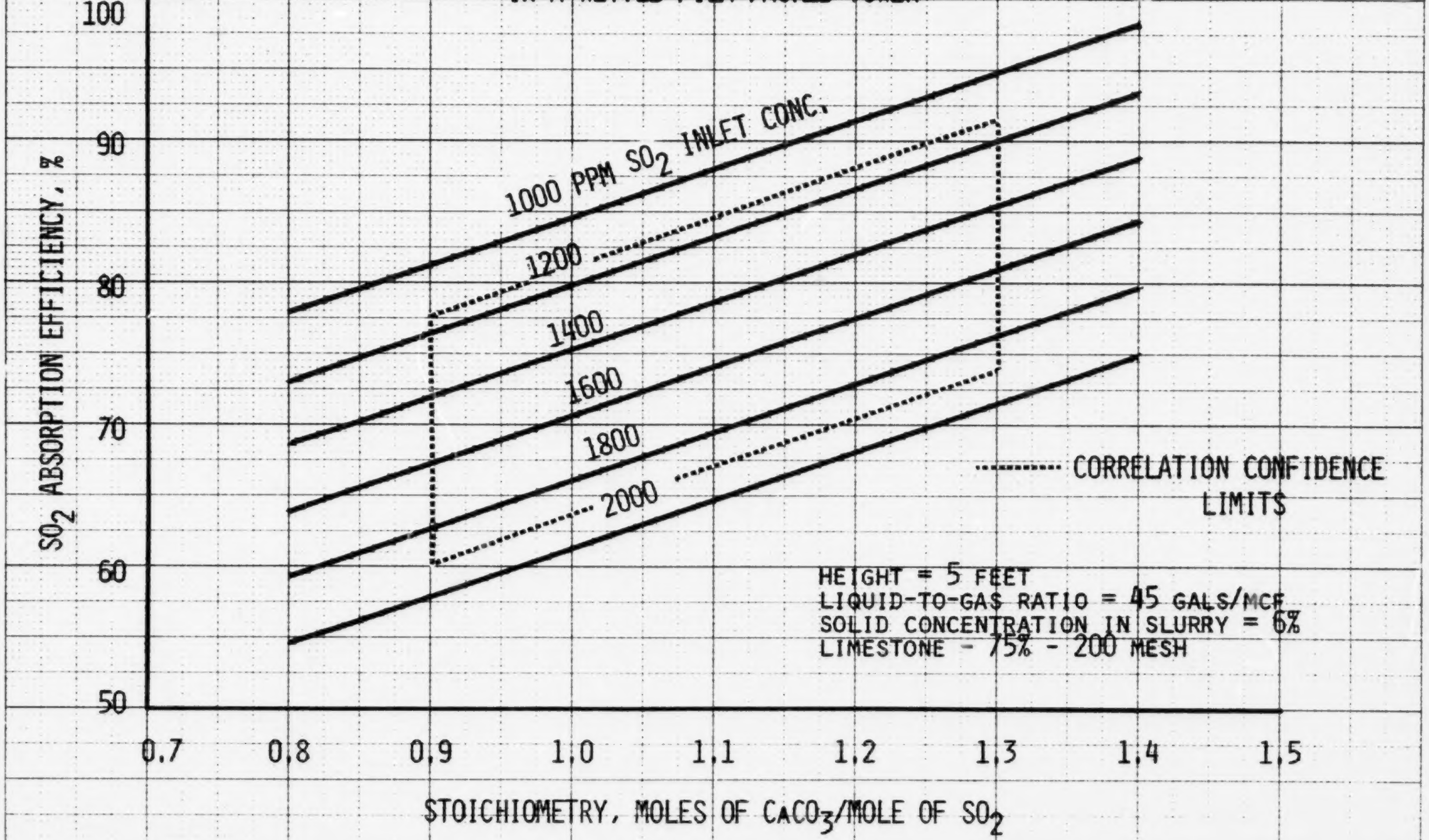
FIGURE IV-1

SULFUR DIOXIDE ABSORPTION WITH LIMESTONE SLURRY
IN A WETTED FILM PACKED TOWER



As the graph illustrates, the efficiency is very sensitive to the stoichiometry and the inlet SO_2 concentration. For a stoichiometric addition of limestone, SO_2 removal can vary between 85 and 62% as the inlet SO_2 concentration changes from 1000 to 2000 ppm. This effect on inlet concentration indicates a significant liquid-phase resistance. It is evident in equation (IV-1) and (IV-2) that the total solid concentration has an adverse effect on the absorption efficiency. This is logical in that the viscosity and flow characteristics would change with increasing solid concentration. A similar slurry influence was observed by Chertkov with hydrated lime slurries in a board packing.[7] He observed decreasing mass-transfer coefficients as a slurry concentration increased.

Simultaneous to this negative coefficient for slurry concentration (SL), the residual calcium carbonate in slurry shows a positive coefficient. Hence, with increasing calcium carbonate concentration, the absorption efficiency improves. The net result of increasing or decreasing the slurry concentration must be analyzed and the effects of total slurry and calcium carbonate concentration should be taken into consideration.

The absorption efficiency for the two limestone grinds, 61% and 75%-200 mesh, showed a considerable difference in absorption efficiency. For a limestone feed of 120% of stoichiometric and a SO_2 inlet concentration of approximately 1300 parts per million, the absorption efficiency expected with the 61%-200 mesh would be approximately 77%. On the other hand, the 75%-200 mesh material for the same conditions would allow near 85% removal. These differences in efficiencies are demonstrated graphically in Figure IV-2. The curves shown

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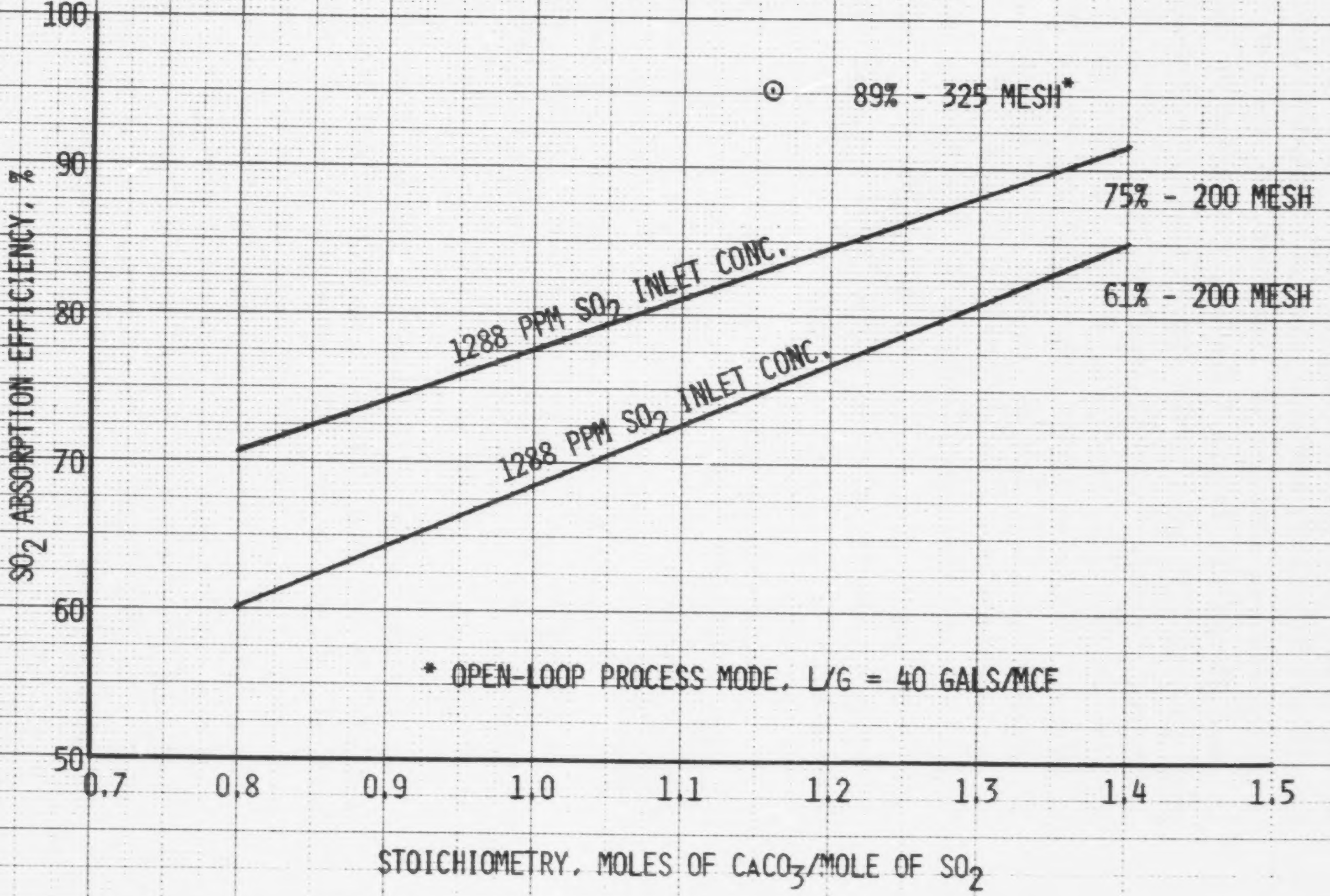
FIGURE IV-2

SULFUR DIOXIDE ABSORPTION WITH LIMESTONE
SLURRY IN A WETTED FILM PACKED TOWER



* OPEN-LOOP PROCESS MODE, L/G = 40 GALS/MCF

represent the expected absorption for a gas containing 1288 ppm SO_2 inlet concentration and a total slurry concentration of 6%.

To illustrate further the influence of the limestone grind, a single point measurement for 89%-325 mesh was also plotted in Figure IV-2. The finer material allowed approximately 11 to 12% more SO_2 removal for the same operating conditions as the 75%-200 mesh. One could conclude from these results that the surface area available for limestone dissolution within the slurry tank and tower and absorber played an important role in the overall mass-transfer resistance.

V. SUMMARY AND CONCLUSIONS

1. A limestone slurry, circulating through a high specific-surface packed tower can absorb greater than 90% of the flue gas SO_2. Absorption efficiency is adversely affected by increasing SO_2 concentration and by high slurry concentration. SO_2 absorption can be improved by increasing the calcium carbonate slurry concentration in the absorbing liquor.

2. A finely ground limestone (90%-325 mesh) increases the SO_2 absorption by 11 or 12% over a material with (75%-200 mesh). Absorption increases with higher liquor-to-gas ratio in the tower.

3. Scale formation in a limestone/SO_2 scrubbing system can be controlled by maintaining a reaction product slurry in the absorbing liquor and by circulating a high liquid rate.

4. A significant liquid phase resistance exists for the limestone/SO_2 system while absorbing the SO_2 with inlet concentration up to 1,000 ppm.

5. Sulfur dioxide absorption in a venturi type scrubber using limestone absorbate is limited to an efficiency between 10 and 20% for $\Delta p = 7"$ of water.

VI. REFERENCES

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4. Frisch, N. W., "Calculated Flooding Velocities For A Wetted Film Packing and Several Commercial Packings", Cottrell Environmental Systems, Inc., Technical Memorandum TM70-19, December 15, 1970.

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APPENDIX A

TABLE A-1

OPERATING CONDITIONS FOR TASK C-2

Date	1/13	1/14	1/14	1/14	1/14	1/14	1/14	1/14	1/14	1/15	1/15
Time	2130	0100	0300	0600	1000	1200	1420	2030	2300	0100	0330
Limestone Used*	B	B	B	B	B	B	B	B	B	B	B
Gas Flow, cfm	700	700	700	700	700	700	700	700	700	700	700
FDS L/G ratio, gal/mcf	10	10	10	10	10	10	10	10	10	10	10
Tower L/G ratio, gal/mcf	30	30	30	30	30	30	30	30	30	30	30
Gas velocity FDS, ft/sec. ***	110	115	130	137	108	--	110	115	116	98	88
Gas velocity Tower, ft/sec.	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35
Tower pressure drop, inches H_2O	1.2	2.2	2.2	3.6	4.3	6.0	7.0	8	6.8	6.0	13.2
FDS pressure drop, inches H_2O	6.9	7.0	7.0	7.0	7.0	6.8	8.0	7.0	6.9	7.0	7.0
CaO/SO_2 ratio (inlet analysis)	1	0.6	1	1	0.9	--	1	1.7**	1.0	1.1	1.1
SO_2 Concentration, ppm											
FDS in ****	1350	1580	1500	1550	1930	1500	1325	1032	1063	1030	1030
FDS out	1525	1600	1550	1230	--	1560	1500	1225	1250	875	950
Tower out	695	1020	880	850	1050	660	336	520	570	320	460
Fraction of SO_2 removed, %											
FDS	--	--	--	--	--	--	--	--	--	15.1	8.8
Tower	54.5	36.3	43.3	30.9	--	57.7	77.6	57.6	54.4	63.5	51.6
Overall	--	--	--	--	45.6	--	--	--	--	69.9	55.4
Gas temperatures, °F											
FDS in	329	342	350	350	349	--	345	340	335	338	335
FDS out	118	122	122	120	122	--	122	120	122	120	110
Tower out	111	110	112	112	--	--	115	116	118	110	102
Liquid temperatures, °F											
FDS in	110	122	122	122	110	--	105	116	115	112	110
FDS out	115	122	120	120	122	--	121	120	120	120	115
Tower in	115	122	120	115	119	--	118	118	120	115	108
Tower out	115	120	118	120	122	--	120	118	118	118	110
PH measurements											
Tower outlet	4.8	4.6	4.8	4.6	4.8	--	5.2	5.6	5.2	4.9	4.2
FDS outlet	6.3	6.2	6.4	6.5	6.4	--	5.3	6.6	6.6	6.5	6.4
Hold tank	5.3	5.0	5.2	5.2	5.9	--	5.5	5.2	5.5	5.6	5.4
Clarifier tank	4.7	4.6	4.6	4.6	4.8	--	4.7	4.7	4.7	4.7	4.6

*Limestone received from TVA for the "around-the-clock" tests designated as A; Old Tiftona from TVA shown as Type B.

**Stoichiometry was 1.0 at 2015

***FDS gas velocity based on outlet gas volume.

**** Some difficulties in SO_2 analyses were experienced during this test High efficiencies and negative absorption on FDS should not be considered valid.

TABLE A-1 cont'd

OPERATING CONDITIONS FOR TASK C-3

Date	1/11	1/12	1/12	1/12	1/13
Time	1600	0930	1730	2230	0100
Limestone Used*	A	A	A	A	A
Gas Flow, cfm	700	700	700	700	700
FDS L/G ratio, gal/mcf	10	10.0	10.3	11	--
Tower L/G ratio, gal/mcf	50	45.5	61.0	40	--
Gas velocity FDS, ft/sec.***	76	76	76	76	76
Gas velocity tower, ft/sec.	8.35	8.35	8.35	8.35	8.35
Tower pressure drop, inches H_2O	1.0	1.0	1.0	1.2	1.7
FDS pressure drop, inches H_2O	--	5	4.9	4.4	4.4
CaO/SO_2 ratio (inlet analysis)	1	1	1	1	1
SO_2 concentration, ppm					
FDS in****	--	1350	1825	1920	2000
FDS out	--	500	1725	733	--
Tower out	--	150	625	429	500
Fraction of SO_2 removed, %					
FDS	--	63.0	2.2	61.9	--
Tower	--	60.0	65.0	41.5	--
Overall	--	88.9	65.8	77.7	75.0
Gas temperatures, °F					
FDS in	--	330	342	364	342
FDS out	--	125	122	122	122
Tower out	--	127	118	121	118
Liquid temperatures, °F					
FDS in	--	130	122	122	122
FDS out	--	122	122	122	122
Tower in	--	12	118	121	120
Tower out	--	125	121	122	122
pH measurements					
Tower outlet	--	6.0	5.2	5.6	5.3
FDS outlet	--	4.0	4.4	4.1	3.8
Hold tank	--	6.3	5.6	5.7	5.4
Clarifier tank	--	--	5.2	5.1	5.0
Hold tank volume	600	600	760	700	700

*Limestone received from TVA for the "around-the-clock" tests designated as A Old Tiftona from TVA shown as Type B

***FDS gas velocity based on outlet gas volume.

**** Some difficulties in SO_2 analyses were experienced during this test. High efficiencies and negative absorption on FDS should not be considered valid.

TABLE A-1 cont'd

OPERATING CONDITIONS FOR TASK C-4

Date	1/18	1/18	1/18	1/18	1/18	1/19	1/19	1/19	1/19	1/19	1/19
Time	1330	1700	1900	2130	2330	0130	0530	1030	1440	1600	2230
Limestone Used	B	B	B	B	B	B	B	B	B	B	B
Gas Flow, cfm	700	700	700	700	700	700	700	700	700	700	700
FDS L/G ratio, gal/mcf	10	10	10	10	10	10	10	10	10	10	10
Tower L/G ratio, gal/mcf	40	40	40	40	40	40	40	40	40	40	40
Gas velocity FDS, ft/sec.***	138	138	138	138	138	138	138	138	138	138	138
Gas velocity Tower, ft/sec.	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35
Tower pressure drop, inches H_2O	--	0.8	0.5	0.7	0.7	0.7	0.7	0.8	1.4	1.2	0.9
FDS pressure drop, inches H_2O	--	7.8	6.4	7.0	7.0	7.0	7.0	7.8	7.9	7.2	7.0
CaO/SO_2 ratio	--	1.6	1.0	.9	1.0	0.9	1.2	0.9	0.9	1.4	--
SO_2 Concentration, ppm											
FDS in ****	--	1150	1750	1700	1325	1230	950	1250	--	1350	1475
FDS out	--	1390	1900	1900	1500	1250	1025	1500	--	1350	1400
Tower out	--	400	150	1125	320	350	488	--	700	680	800
Fraction of SO_2 removed, %											
FDS	--	--	--	--	--	--	--	--	--	--	5.1
Tower	--	71.3	92.2	40.8	78.7	72.0	52.4	--	--	49.7	42.9
Overall	--	--	--	--	--	--	--	--	--	--	45.8
Gas temperatures, °F											
FDS in	--	335	335	330	330	330	330	335	330	333	338
FDS out	--	110	90	105	105	105	105	115	110	112	112
Tower out	--	105	80	100	100	100	102	105	105	105	105
Liquid temperatures, °F											
FDS in	--	112	100	105	105	105	105	112	110	112	108
FDS out	--	125	120	115	110	110	112	120	118	120	120
Tower in	--	108	83	100	100	100	100	105	105	105	105
Tower out	--	111	100	110	-	110	110	-	-	112	-
pH measurements											
Tower outlet	--	4.9	5.7	5.5	5.2	5.3	4.2	4.7	4.9	4.9	4.8
FDS outlet	--	6.6	6.9	7.0	5.4	7.2	7.4	6.7	6.3	6.7	6.5
Hold tank	--	5.6	6.3	5.7	5.7	5.9	5.8	5.7	5.5	5.5	5.5
Clarifier tank	--	7.1	7.1	7.1	7.1	7.2	-	-	-	-	-

***FDS gas velocity based on outlet gas volume.

**** Some difficulties in SO_2 analyses were experienced during this test. High efficiencies and negative absorption on FDS should not be considered valid.

TABLE A-1 cont'd

OPERATING CONDITIONS FOR TASK C-4

Date	1/19	1/20	1/20
Time	2230	0330	0330
Limestone Used	B	B	B
Gas Flow, cfm	700	700	700
FDS L/G ratio, gal/mcf	10	10	10
Tower L/G ratio, gal/mcf	40	40	40
Gas velocity FDS, ft/sec.***	138	138	138
Gas velocity Tower, ft/sec.	8.35	8.35	8.35
Tower pressure drop, inches H_2O	1.6	1.6	1.6
FDS pressure drop, inches H_2O	7.0	7.0	7.0
CaO/SO_2 ratio	--	1.0	--
SO_2 Concentration, ppm			
FDS in ****	1650	850	500
FDS out	1625	702	425
Tower out	1040	400	100
Fraction of SO_2 removed, %			
FDS	1.6	17.4	15.0
Tower	36.0	42.4	76.5
Overall	37.0	52.9	80.0
Gas temperatures, °F			
FDS in	325	332	325
FDS out	110	105	100
Tower out	103	104	98
Liquid temperatures, °F			
FDS in	105	102	102
FDS out	120	112	112
Tower in	105	102	102
Tower out	-	102	-
pH measurements			
Tower outlet	4.7	4.6	-
FDS outlet	7.1	6.4	-
Hold tank	5.3	5.4	-
Clarifier tank	-	-	-

***FDS gas velocity based on outlet gas volume.

**** Some difficulties in SO_2 analyses were experienced during this test. High efficiencies and negative absorption on FDS should not be considered valid.

TABLE A-1 cont'd

OPERATING CONDITIONS FOR TASK C-5

Date	1/20	1/20	1/20	1/20	1/20	1/20	1/20	1/21	1/21	1/21	1/21	1/21
Time	1130	1230	1400	1700	1900	2100	2300	0100	0300	0500	0730	0915
Limestone Used	B	B	B	B	B	B	B	B	B	B	B	B
Gas Flow, cfm	700	700	700	700	700	700	700	700	700	700	700	700
FDS L/G ratio, gal/mcf	10	10	10	10	10	10	10	10	10	10	10	10
Tower L/G ratio, gal/mcf	40	40	40	40	40	40	40	40	40	40	40	40
Gas velocity FDS, ft/sec.***	141	141	141	141	141	141	141	141	115	115	138	108
Gas velocity Tower, ft/sec.	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35
Tower pressure drop, inches H_2O	0.8	1.0	1.0	0.8	1.1	1.1	1.1	1.1	1.9	1.9	3.1	5.4
FDS pressure drop, inches H_2O	6.6	6.4	7.2	6.6	7.2	6.7	7.0	7.0	7.0	7.0	7.0	5.8
CaO/SO_2 ratio	--	--	1.1	1.1	2.1	1.4	1.1	2.0	1.7	1.45	--	1.45
SO_2 Concentration, ppm												
FDS in ****	1250	1075	1050	950	850	750	850	775	600	500	600	750
FDS out	800	600	425	350	300	250	300	378	250	234	300	275
Tower out	17	200	235	100	185	155	285	330	160	125	150	120
Fraction of SO_2 removed, %												
FDS	36.0	44.2	59.5	63.1	64.7	66.6	64.7	51.3	58.3	53.2	50.0	63.3
Tower	97.8	66.7	44.7	71.4	38.3	38.0	5.00	12.7	36.0	53.4	50.0	54.6
Overall	98.6	81.4	77.6	89.4	78.3	79.3	66.5	57.4	73.4	75.0	75.0	84.0
Gas temperatures, °F												
FDS in	335	330	330	330	333	332	328	330	332	332	--	335
FDS out	85	108	110	105	115	115	117	118	112	110	--	115
Tower out	70	102	105	102	112	112	113	112	112	105	--	110
Liquid temperatures, °F												
FDS in	100	105	105	105	108	111	112	110	108	102	--	85
FDS out	110	115	115	115	118	118	118	118	118	126	--	--
Tower in	75	102	105	100	112	112	115	115	112	106	--	110
Tower out	80	105	110	105	115	115	118	118	118	-	--	--
pH measurements												
Tower outlet	5.6	5.0	5.2	4.8	5.1	4.5	5.3	4.6	5.0	4.8	--	4.8
FDS outlet	5.0	6.0	4.9	5.2	4.9	4.9	4.8	4.8	4.8	4.7	--	4.3
Hold tank	6.3	7.1	6.2	6.4	6.6	6.4	6.4	6.2	6.4	6.0	--	5.7
Clarifier tank	--	--	--	--	6.4	5.9	5.7	5.6	5.5	5.5	--	4.3

***FDS gas velocity based on outlet gas volume.

**** Some difficulties in SO_2 analyses were experienced during this test. High efficiencies and negative absorption on FDS should not be considered valid.

TABLE A-1 cont'd

OPERATING CONDITIONS FOR TASK C-5

Date	1/21	1/21	1/21	1/21	1/21	1/21	1/21
Time	1100	1300	1500	1700	1900	2100	2300
Limestone Used	B	B	B	B	B	B	B
Gas Flow, cfm	700	700	700	700	700	700	700
FDS L/G ratio, gal/mcf	10	10	10	10	10	10	10
Tower L/G ratio, gal/mcf	40	40	40	40	40	40	40
Gas velocity FDS, ft/sec.***	111	132	115	115	115	115	115
Gas velocity Tower, ft/sec.	8.35	8.35	8.35	8.35	8.35	8.35	8.35
Tower pressure drop, inches H_2O	5.0	5.0	3.2	3.3	3.6	3.9	4.3
FDS pressure drop, inches H_2O	5.8	6.0	5.2	4.6	4.2	4.6	4.0
CaO/SO_2 ratio	1.27	1.3	0.8	1.0	0.9	0.9	0.9
SO_2 Concentration, ppm							
FDS in ****	825	890	1125	1300	1500	1600	1650
FDS out	225	225	1050	1250	1375	1550	1525
Tower out	210	240	330	370	355	425	360
Fraction of SO_2 removed, %							
FDS	72.8	74.8	7.7	5.7	8.4	3.1	7.6
Tower	6.7	--	68.6	70.4	74.2	72.6	76.4
Overall	74.6	73.1	70.7	71.6	76.4	73.5	78.2
Gas temperatures, °F							
FDS in	335	340	335	335	335	335	333
FDS out	120	115	120	118	119	121	120
Tower out	115	70	120	119	119	120	120
Liquid temperatures, °F							
FDS in	110	105	118	114	115	118	118
FDS out	-	115	120	118	118	120	119
Tower in	120	115	120	119	119	121	121
Tower out	-	--	--	--	--	--	--
pH measurements							
Tower outlet	4.9	4.8	3.0	3.8	5.9	5.8	5.3
FDS outlet	4.5	3.7	3.7	4.1	4.6	4.9	5.1
Hold tank	5.7	5.4	5.7	5.8	6.2	6.0	5.9
Clarifier tank	5.2	5.1	5.0	4.8	4.2	4.2	4.2

*** FDS gas velocity based on outlet gas volume.

**** Some difficulties in SO_2 analyses were experienced during this test. High efficiencies and negative absorption on FDS should not be considered valid.

TABLE A-1 cont'd

OPERATING CONDITIONS FOR TASK C-6

Date	1/25	1/25	1/25	1/26	1/26	1/26	1/26	1/26	1/26	1/26	1/27
Time	1830	2130	2400	0200	0400	1115	1230	1500	1715	2230	0300
Limestone Used	B	B	B	B	B	B	B	B	B	B	B
Gas Flow, cfm	700	700	700	700	700	700	700	700	700	700	700
FDS L/G ratio, gal/mcf	10	10	10	10	10	10	10	10	10	10	10
Tower L/G ratio, gal/mcf	45	45	45	45	45	45	45	45	45	45	45
Gas velocity FDS, ft/sec.***	127	141	141	141	141	141	135	135	135	141	141
Gas velocity Tower, ft/sec.	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35
Tower pressure drop, inches H_2O	1.0	1.0	1.1	0.9	1.0	1.0	1.0	1.0	0.9	0.9	0.9
FDS pressure drop, inches H_2O	6.4	7.0	6.5	6.8	7.3	6.0	6.2	5.8	6.2	7.0	7.0
CaO/SO_2 ratio	0.9	1.0	0.9	1.0	1.0	1.0	1.2	1.2	0.9	1.1	0.9
SO_2 Concentration, ppm											
FDS in	1700	1700	1920	1930	1890	1680	1360	1260	1380	1400	1565
FDS out	1580	1635	1900	1760	1735	1560	1220	1160	--	1320	1440
Tower out	540	620	880	560	460	320	100	34	--	240	280
Fraction of SO_2 removed, %											
FDS	7.1	3.9	1.0	8.8	8.2	7.2	10.3	8.0	--	5.8	8.0
Tower	65.9	62.1	53.7	68.2	73.5	79.5	91.8	97.1	--	81.9	80.6
Overall	68.3	63.5	54.2	71.0	75.7	81.0	92.7	97.4	--	82.9	82.2
Gas temperatures, °F											
FDS in	335	328	335	330	330	--	--	330	335	333	335
FDS out	105	120	120	118	120	118	118	118	118	118	115
Tower out	108	120	120	118	120	118	118	118	115	115	116
Liquid temperatures, °F											
FDS in	40	114	112	115	118	112	112	112	110	114	114
FDS out	85	118	120	118	120	120	120	120	118	118	118
Tower in	108	118	121	118	120	118	118	118	115	115	114
Tower out	108	118	121	120	122	118	120	120	118	118	118
pH measurements											
Tower outlet	5.4	5.4	4.9	5.2	5.4	5.5	5.9	6.6	4.3	5.7	4.8
FDS outlet	4.6	4.4	5.2	5.0	4.8	5.4	6.8	6.8	6.6	4.8	4.8
Hold tank	5.3	5.5	5.3	5.7	5.4	6.2	6.4	6.1	6.0	6.4	6.3
Clarifier tank	3.2	3.4	3.4	4.7	4.6	4.3	4.5	4.9	4.9	4.6	4.5

***FDS gas velocity based on outlet gas volume.

TABLE A-1 cont'd

OPERATING CONDITIONS FOR TASK C-6

Date	1/29	1/29	1/29	1/30	1/30	1/30	1/30	1/30	1/30	1/30	1/30	1/30	1/31
Time	1405	1620	2100	0200	0600	1230	1330	1415	1505	1830	2100	2330	0100
Limestone Used	A	A	A	A	A	A	A	A	A	A	A	A	A
Gas Flow, cfm	700	700	700	700	700	700	700	700	700	700	700	700	700
FDS L/G ratio, gal/mcf	10	10	10	10	10	10	10	10	10	10	10	10	10
Tower L/G ratio, gal/mcf	45	45	45	45	45	45	45	45	45	45	45	45	45
Gas velocity FDS, ft/sec.***	127	127	127	141	141	151	141	141	141	141	141	141	141
Gas velocity Tower, ft/sec.	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35	8.35
Tower pressure drop, inches H_2O	0.8	0.8	0.8	0.7	0.6	0.6	--	--	0.6	1.1	1.1	0.9	0.9
FDS pressure drop, inches H_2O	6.4	7.0	7.0	7.0	7.0	6.4	--	--	6.0	7.2	7.6	6.4	7.0
CaO/SO_2 ratio	1.2	1.2	1.2	1.2	1.1	1.3	1.2	1.2	1.2	1.2	1.2	1.2	1.2
SO_2 Concentration, ppm													
FDS in	1440	1440	1360	1280	1480	1450	1420	1240	1260	1160	1000	1000	1080
FDS out	1320	1340	1280	1140	1380	1340	1300	--	1120	1100	960	979	1000
Tower out	360	220	210	280	280	400	320	120	140	84	20	20	72
Fraction of SO_2 removed, %													
FDS	8.4	8.0	5.9	11.0	6.8	7.6	8.5	--	11.2	5.2	4.0	4.0	2.9
Tower	72.8	83.5	83.6	75.5	79.8	70.2	75.4	--	87.5	92.4	97.9	97.9	92.8
Overall	75.0	84.8	84.6	78.2	81.1	72.5	77.5	90.4	88.9	92.8	98.0	98.0	93.3
Gas temperature, °F													
FDS in	342	340	342	335	330	325	--	--	330	330	320	325	330
FDS out	122	112	122	120	120	120	--	--	120	116	120	118	118
Tower out	122	110	120	118	118	120	--	--	118	112	118	112	112
Liquid temperatures, °F													
FDS in	119	100	118	118	116	118	--	--	115	115	114	115	116
FDS out	126	118	125	122	122	122	--	--	122	122	120	121	120
Tower in	122	112	121	118	118	120	-	--	118	113	120	112	114
Tower out	125	115	123	120	120	122	--	--	122	118	120	118	120
pH measurements													
Tower outlet	5.8	3.5	5.8	5.6	5.4	5.4	--	--	5.5	5.1	5.3	4.4	4.8
FDS outlet	5.4	4.2	5.4	5.4	4.7	5.5	--	--	6.0	4.4	4.4	4.0	4.9
Hold tank	7.6	5.4	5.4	6.2	6.2	5.8	--	--	6.2	6.4	6.3	6.2	6.0
Clarifier tank	3.6	5.0	5.0	5.2	4.9	5.2	--	--	5.2	5.1	4.9	5.0	5.0

***FDS gas velocity based on outlet gas volume.

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY:

TVA PILOT PLANT TESTS

I. SCRUBBER-TYPE COMPARISON

By

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II. EXPERIMENTAL DESIGN AND DATA ANALYSIS FOR SPRAY AND MOBILE-BED SCRUBBERS

By

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New Orleans, Louisiana
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REMOVAL OF SULFUR DIOXIDE FROM STACK GASES
BY SCRUBBING WITH LIMESTONE SLURRY:
TVA PILOT PLANT TESTS

ABSTRACT

I. SCRUBBER-TYPE COMPARISON

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TVA plans to install limestone slurry scrubbing on a 500-mw boiler (No. 8 unit at the Widows Creek station) as a demonstration project. Since adequate design data for limestone scrubbing are not available, a pilot plant (2000-cfm capacity) has been constructed at the Colbert Steam Plant and operated for about 10 months. The limestone, pulverized to about 70% minus 200 mesh, is a high-calcium type from the Widows Creek area. Most of the tests have been at a $CaO:SO_2$ mole ratio of 1.5, an L/G (gal slurry/Mcf of gas) of 50 to 60, and a slurry solids content of 10-15%; the stack gas contains about 3000 ppm of SO_2. All long-term tests have been with a closed-liquor loop.

Since others have shown that packed scrubbers are effective contactors but subject to scaling, three scrubber types were tested--ranging from fully packed (with fixed packing) to an empty tower. These systems were:

1. Ventri-Rod (a type of venturi) followed by a packed crossflow scrubber.
2. Three-stage mobile-bed scrubber (bouncing bed of hollow plastic balls).
3. Ventri-Rod followed by open spray tower.

With the Ventri-Rod - packed crossflow scrubber configuration, about 80% of the SO_2 was removed from the gas stream. This system could not be operated for more than about 120 hours because of plugging of the packing either by deposition of slurry solids or by scaling.

With the Ventri-Rod - open-spray tower configuration, about 77% of the SO_2 was absorbed. This system was operated continuously without difficulty for over 350 hours and routinely shut down.

Tests are in progress with the mobile-bed scrubber. In the tests that have been completed, 90-92% of the SO_2 in the flue gas has been removed.

Several problems other than scaling have been encountered, including (1) slurry solids deposition on surfaces, (2) poor settling of solids, (3) unstable operation (irreversible decline in pH) under some conditions, (4) corrosion and erosion of surfaces, and (5) mist carryover. All of these have been fairly well resolved (although further improvement would be desirable) except the last two. Test programs aimed specifically at erosion and mist carryover are under way.

The following conclusions can be drawn from these studies:

1. Good absorption (75-90%) can be obtained without scaling if the proper scrubber type is used. Longer test runs are desirable, however, to confirm the nonscaling operation.

2. At the high liquor rates required for SO_2 removal in limestone slurry scrubbing, and for fly ash of the type involved in these tests, excellent collection of the dust in the incoming gas is achieved with no special provisions. Solids carryover in mist is a major problem, however, and must be solved if limestone slurry scrubbing is to be a usable process.

3. Care must be taken to maintain an adequate rate of limestone dissolution in order to avoid unstable operation. Other variables may also be effective in accomplishing this but have not been tested.

II. EXPERIMENTAL DESIGN AND DATA ANALYSIS FOR SPRAY AND MOBILE-BED SCRUBBERS

By

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The experimental designs and statistical analyses of the data from several pilot plant runs on limestone scrubbing are discussed. Scrubber types involved are a mobile bed (three beds of hollow plastic balls) and three configurations of an assembly consisting of a Ventri-Rod followed by sprays in an open tower. The significant variables for each type are identified and linear regression equations derived.

A mathematical model for fly ash removal is developed from data obtained in a mobile-bed scrubber operated at a power plant with water as the scrubbing medium. The fly ash model is compared with experimental data obtained in scrubbing with limestone slurry.

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES BY SCRUBBING WITH LIMESTONE SLURRY: TVA PILOT PLANT TESTS

I. SCRUBBER-TYPE COMPARISON

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In addition to the small-scale work described earlier in this symposium ("Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Small-Scale Studies at TVA" by J. M. Potts, A. V. Slack, and J. D. Hatfield), pilot plant studies on limestone slurry scrubbing have been carried out. The purpose of both studies is to supply information needed for design of the full-scale demonstration scrubbing facility that TVA plans to install on the No. 8 generating unit (550-mw) at the Widows Creek Steam Plant (near Chattanooga, Tennessee). The pilot plant is located at the Colbert Steam Plant (on the No. 3 unit), which is near TVA's chemical research facilities at Muscle Shoals, Alabama.

The main purpose of the pilot plant work has been to identify the problems that affect operational reliability and to find ways of solving them. (Scaling, for example, is known to be a major problem of this type.) Part I of this paper deals mainly with this aspect of the test program. Some effort was also made toward optimizing the operating parameters; Part II covers the experimental design and data analysis associated with this phase of the work.

The pilot plant, which is still in operation, receives a sidestream of gas of about 2000 cfm (measured at scrubber outlet conditions--saturated at 120°F) from the outlet duct of the boiler (Babcock and Wilcox, front-fired, pulverized coal), in which coal containing about 4% S and 15% ash is burned. The stack gas entering the pilot plant contains about 3000 ppm SO_2 and 3 to 4 grains per scf (dry basis) of fly ash.

In the pilot plant the gas is scrubbed with a circulating limestone slurry containing 12 to 15% solids. This level of solids was selected because a higher content increases pumping difficulty and increases settling tendencies in the scrubber; a lower one reduces the beneficial effect of high solids content on scaling and SO_2 removal.

Pulverized limestone is slurried and fed into the liquor circulation loop continuously. Typical analyses of the three limestones used are given in Table I. Preliminary tests in the pilot plant did not indicate any significant difference in the reactivity of the three; consequently, most of the tests were made with limestone from Tiftonia, Tennessee, which is near the Widows Creek Steam Plant.

TABLE I

Typical Limestone Analyses

Quarry location	Chemical analyses, %				Screen analyses, cumulative % retained on		
	CaO	MgO	Al_2O_3	SiO_2	100 mesh	200 mesh	325 mesh
Birmingham, Alabama	53.8	1.2	0.07	1.4	14	28	38
Scottsboro, Alabama	50.0	4.0	0.52	2.2	8	22	37
Tiftonia, Tennessee	52.3	1.2	0.13	3.4	10	27	40

Three different types of scrubbers have been tested; fixed packing, mobile packing, and spray tower. The objective of the tests was to determine which of the three would give the best combination of reliability and SO_2 removal efficiency.

Packed Scrubber (Fixed Packing)

The packed scrubber selected for testing was the crossflow type (Fig 1); the horizontal configuration would have the advantage of fitting better into the duct system from boiler to stack. The scrubber, manufactured by the Ceilcote Company, consisted of a horizontal housing (glass-reinforced plastic) filled with spiral-type polypropylene packing (Tellerettes) irrigated across the top with nozzles set at right angles to the gas flow. A section of the packing at the gas outlet was left unirrigated to serve as an integral entrainment separator.

The crossflow was preceded by a venturi scrubber, the primary function of which was to remove fly ash. The type used was the Ventri-Rod (manufactured by Environeering, Inc.), essentially a horizontal housing containing a "window" section of irrigated parallel rods (3/4-in. diameter; stainless steel) spaced to develop the pressure drop necessary for particulate removal (Fig 2). The pressure drop across the rod section could be adjusted by two guillotine-type movable gates. The rod section was followed by a chevron-type entrainment separator. The entire scrubber, except for the rods, was made of mild steel coated with bitumastic material.

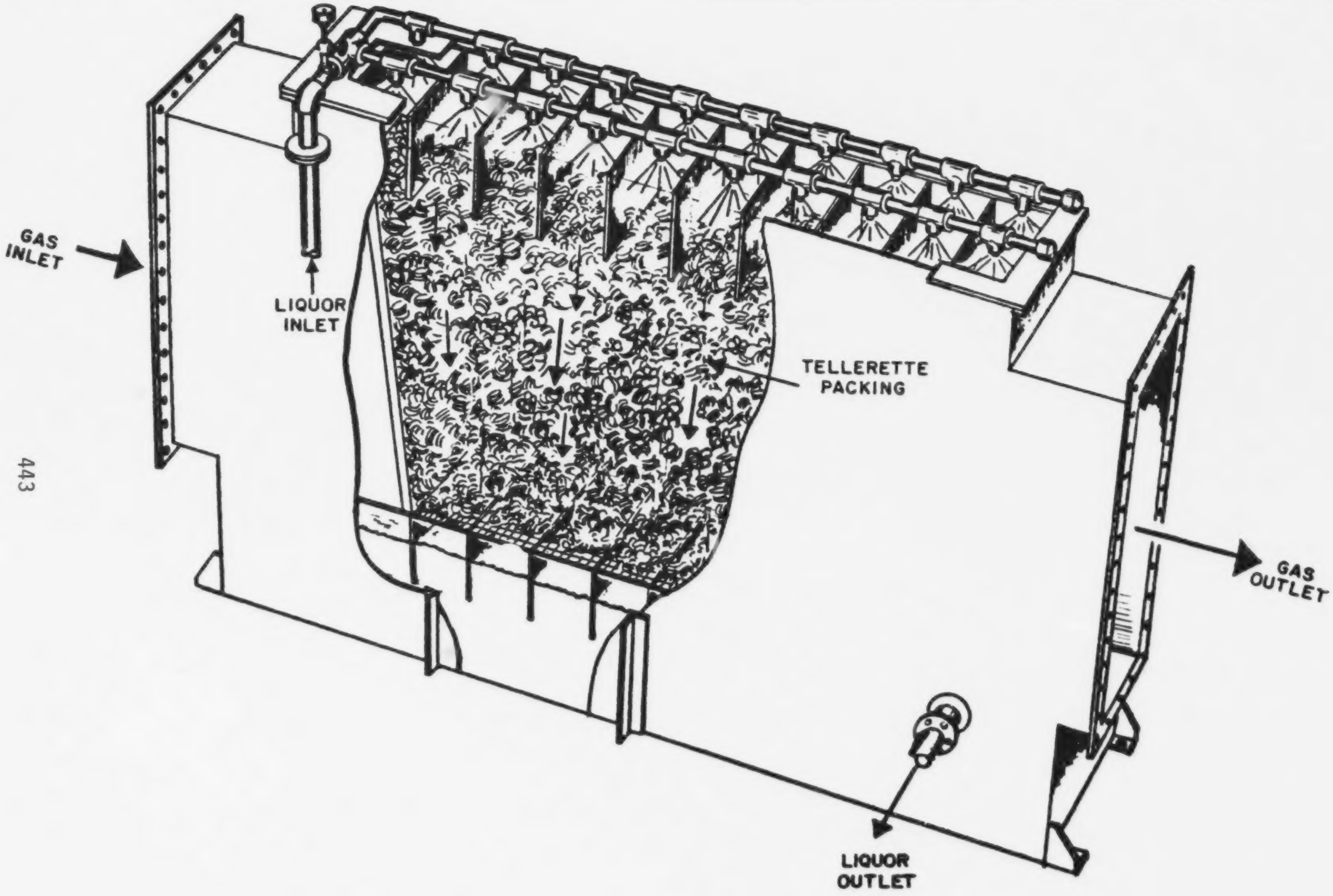

FIGURE 1

Packed Crossflow Scrubber

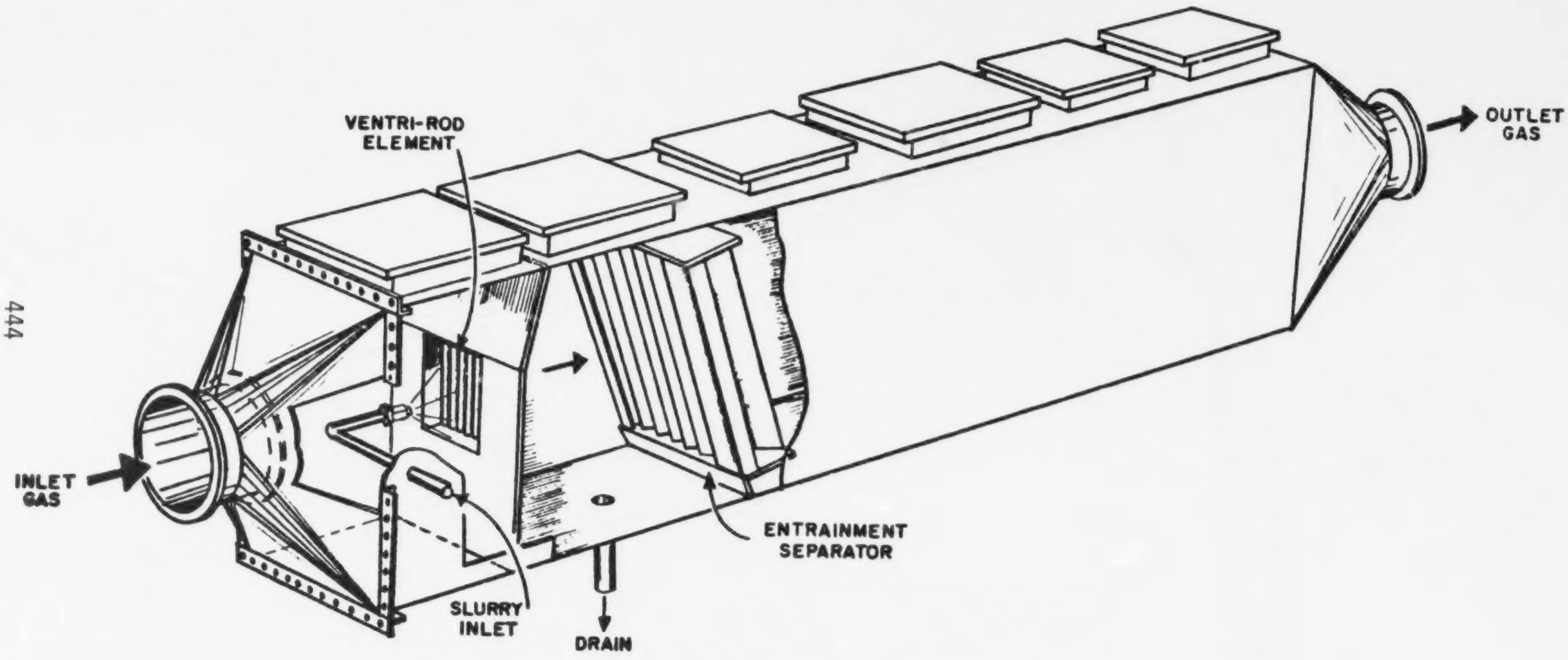

FIGURE 2

Horizontal Ventri-Rod

The overall pilot plant (Fig 3) consisted of the scrubbers connected in series, recirculation tanks equipped with agitators and pumps, settling tanks, and a slurry preparation tank. Separate slurry circulation loops were provided for the two scrubbers. Pulverized limestone was slurried in the slurry preparation tank, with liquor from the recirculation tank in the crossflow scrubber loop, and pumped continuously at a controlled rate back into the tank. From there it was pumped to the scrubber and returned to the tank by gravity. The recirculation tank had a working capacity of about 500 gallons. In most of the tests, the L/G ratio (gal slurry/1000 scf of gas) was maintained at about 40; consequently slurry residence time in the tank was about 6 minutes. This was about twice the retention time used in the ICI-Howden experiments.

Slurry from the crossflow recirculation tank flowed by gravity to the Ventri-Rod recirculation tank. The working capacity of the latter was 500 gallons; at the usual L/G of 15, residence time in the tank was about 17 minutes.

Slurry from the Ventri-Rod tank flowed by gravity to the settling tanks. Supernatant liquor from the settling tanks was returned to the crossflow recirculation tank, at a withdrawal rate regulated to maintain the solids content in the recirculated slurry at 12 to 15%. The product solids and fly ash were periodically pumped from the settling tanks and discarded.

Unstable pH: In preliminary tests with this scrubber configuration, two major problems developed that prevented sustained operation: (1) decline in the pH of the scrubbing slurry finally resulted in an unresponsive slurry and (2) uncontrollable solids buildup in the circulating slurry.

In the initial attempts to start the pilot plant on a continuous multishift operation, the crossflow circulation tank was charged with limestone and water proportioned to form a slurry containing 5% solids. The flow of gas was started through the crossflow scrubber and the slurry circulated from the recirculation tank through the scrubber and back to the tank. No fresh limestone was added to the system until the initial batch of limestone in the slurry was exhausted. A forward flow of slurry to the Ventri-Rod scrubber was then established, the scrubbing loop closed, and the addition of fresh limestone started (stoichiometry, 1.0). The pH of the slurry immediately began to drop, despite the continual addition of fresh limestone, to such an extent that the slurries became completely unresponsive. The pH declined finally to 3.7 and the SO_2 removal decreased to about 30%. Addition of limestone in large quantities to samples of the slurry did not appreciably increase the pH. Electron microscopic analyses indicated that the limestone particles in the slurry were covered with a thin crystalline layer of material which appeared to be calcium sulfite. The layer of sulfite apparently prevented the limestone substrate from further dissolution and reaction.

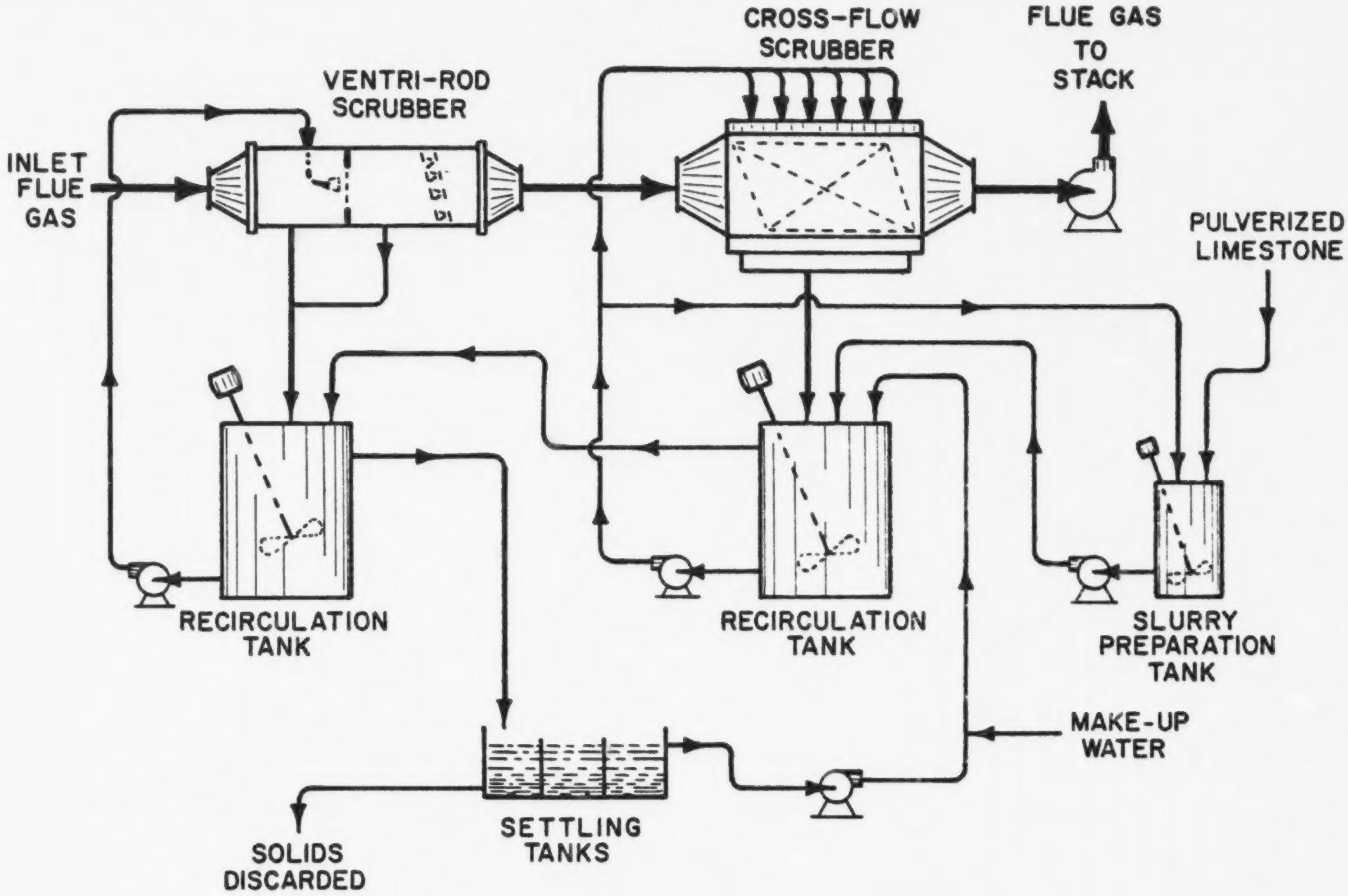

FIGURE 3

Pilot Plant with Ventri-Rod and Crossflow Scrubber Configuration

The mechanism of the limestone blinding is not yet known (see paper in this symposium, "Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Small-Scale Studies at TVA" by J. M. Potts, A. V. Slack, and J. D. Hatfield); however, it is obvious that low pH triggers it. The exact pH at which the slurry becomes irreversibly unresponsive has not been clearly defined but there is some indication from the pilot plant work that if a level no lower than 4.5 can be maintained, the slurry will return to full responsiveness.

If the pH falls below about 4.0, the pH cannot be restored by any procedure practical in large plant operation, and the slurry must be discarded.

The procedure developed to maintain pH at a high level during startup involved filling the circulation tanks with fresh limestone slurry and then starting the forward feed flow, slurry circulation, and limestone feed simultaneously with the flow of gas. Consequently, during the initial startup period before plant operation was stabilized the circulating slurries contained a large excess of limestone. Moreover, the stoichiometry was increased to 1.5 in an effort to maintain a stable pH.

Even with a large excess of limestone in the scrubbing circuits, the pH of the slurries and the removal of SO_2 tended to decline during the first 20 to 30 hours of operation. After this initial period, however, there was a rapid increase and then stabilization. This phenomenom may be a function of the ionic strength of the circulating slurry. A typical decline and recovery is shown in Figure 4.

Unstable pH also occurred in two other tests in which the plant had to be shut down for a period of about 1 hour during each test for emergency maintenance. The flow of slurry to the crossflow scrubber was maintained during the shutdown to prevent drying out of the packing. During both periods, a small amount of flue gas (estimated to be 300 cfm) leaked through the scrubber. Even this small amount of gas depleted the alkalinity of the slurry and made it necessary to abort one of the tests because the slurry had become completely unresponsive. In the second test, lime was added to the scrubber slurry to raise the pH to about 5.0 in the crossflow scrubber loop and 4.8 in the Ventri-Rod loop. The pH rapidly dropped back to about 4.0 and remained in the range of 4.0 to 4.5 for several hours. After approximately 7 hours of operation, the pH of the makeup limestone slurry (made with circulation tank liquor) increased from 4.5 to 6.1 within an hour. After 3 hours of additional operation, the pH of the slurry to the crossflow scrubber increased from 4.2 to 5.0 within an hour and immediately the removal of SO_2 increased from 49 to 80% (Table II).

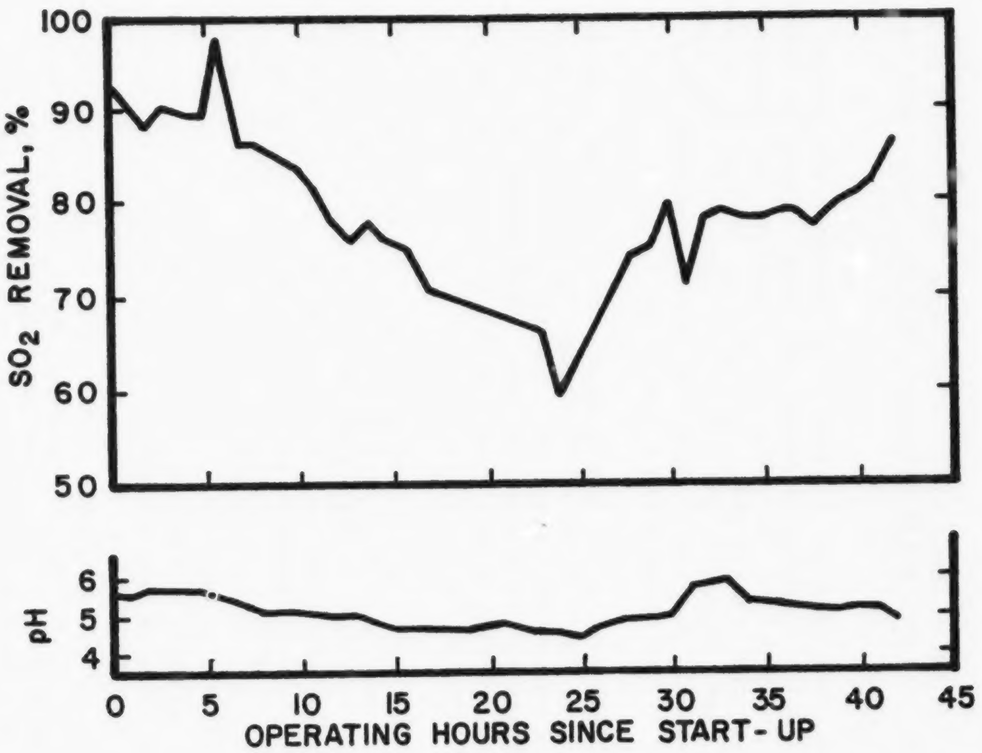

FIGURE 4

SO_2 Removal and pH in Crossflow Recirculation Liquor

TABLE II

Sulfur Dioxide Removal and Liquor pH's Before and After Increase in Sulfur Dioxide Removal

			pH of liquor, from		
March	Time	SO_2 removal, %	F-11 Mixing tank	F-12 Crossflow	F-13 Ventri-Rod
17	5 p.m.	34	4.7	4.1	4.2
	6 p.m.[a]	59	4.6	4.5	4.6
	7 p.m.	64	6.6	4.4	4.5
	8 p.m.	49	6.1	4.3	4.3
	9 p.m.	50	5.5	4.2	4.3
	10 p.m.	48	6.8	4.2	4.3
	11 p.m.	47	4.7	4.3	4.3
	12 p.m.	45	4.6	4.0	4.1
18	1 a.m.	46	4.5	4.0	4.2
	2 a.m.	47	6.1	4.1	4.2
	3 a.m.	50	6.0	4.2	4.3
	4 a.m.	49	6.1	4.2	4.4
	5 a.m.	80	6.5	5.0	4.3
	6 a.m.	86	6.8	5.1	4.6
	7 a.m.	87	6.8	5.2	4.5
	8 a.m.	84	6.5	5.8	4.9
	9 a.m.	83	6.8	5.6	4.9
	10 a.m.	83	6.7	5.4	4.9
	11 a.m.	82	6.7	5.5	4.9
	12 m.	77	6.9	5.4	4.9
	1 p.m.	77	6.7	5.4	4.9
	2 p.m.	76	6.6	5.6	5.0
	3 p.m.	78	6.8	5.4	4.9

---

[a] Lime added: 40 lb to circulation tank of crossflow scrubber and 20 lb to circulation tank of Ventri-Rod.

The combination of high initial limestone content in the slurry and a continuing makeup at 1.5 times stoichiometric made it possible to operate without trouble from unstable pH. Lower stoichiometry may be feasible but has not yet been adequately demonstrated.

Solids Settling Rate: The second problem that prevented sustained operation in the preliminary tests was the uncontrollable solids buildup in the circulating slurry. In the original pilot plant configuration, the settling tanks had a total capacity of about 800 gallons but due to the slow settling characteristics of the slurry, the resulting 3-1/2 hours' retention time was inadequate. The solids content in the slurry would increase linearly from about 5% in the starting slurry to approximately 25 to 30% after about 30 hours of operation, a level that caused plugging of the packing in the crossflow scrubber.

The settling tank was replaced with three tanks having a usable capacity of about 4,000 gallons, equivalent to about 20 hours' retention time. In subsequent tests with the additional settling capacity, the solids content of the slurry could easily be controlled at the desired 12 to 15% level.

Although the additional settling time made it possible to operate the pilot plant satisfactorily in these and the later tests, settling remains a problem. Even after several weeks, the settled solids layer contains only about 40% solids and the volume occupied in a waste pond therefore would be relatively large. Tests on methods for getting a more compact settled layer are planned.

Scaling: Because of the uncontrolled pH decline and the buildup of solids, the initial pilot plant tests were usually of only 30 to 40 hours' duration. After these problems were corrected, attempts were made to operate the pilot plant for longer periods. The longest period of sustained operation (about 125 hr) was terminated because of scaling of the scrubber packing.

Before this test was made, the packing was removed from the crossflow scrubber and cleaned. At the outset of the test, the pressure drop across the scrubber was 4 in. H_2O. There was a steady increase during the test until after 125 hr of operation (Fig 5) the pressure drop exceeded 17 in., which caused the seals in the scrubber sump to blow. Many of the Tellerettes were cemented together into a large mass by a hard, tenacious scale. Also, much of the open area in the individual Tellerettes was blocked or obstructed by the scale formation.

Several attempts were made to wash the packing in place with high-velocity streams of water. Practically none of the tightly adhering scale could be dislodged. The packing was removed, new packing installed, and the test resumed. The results were essentially the same as in the previous test.

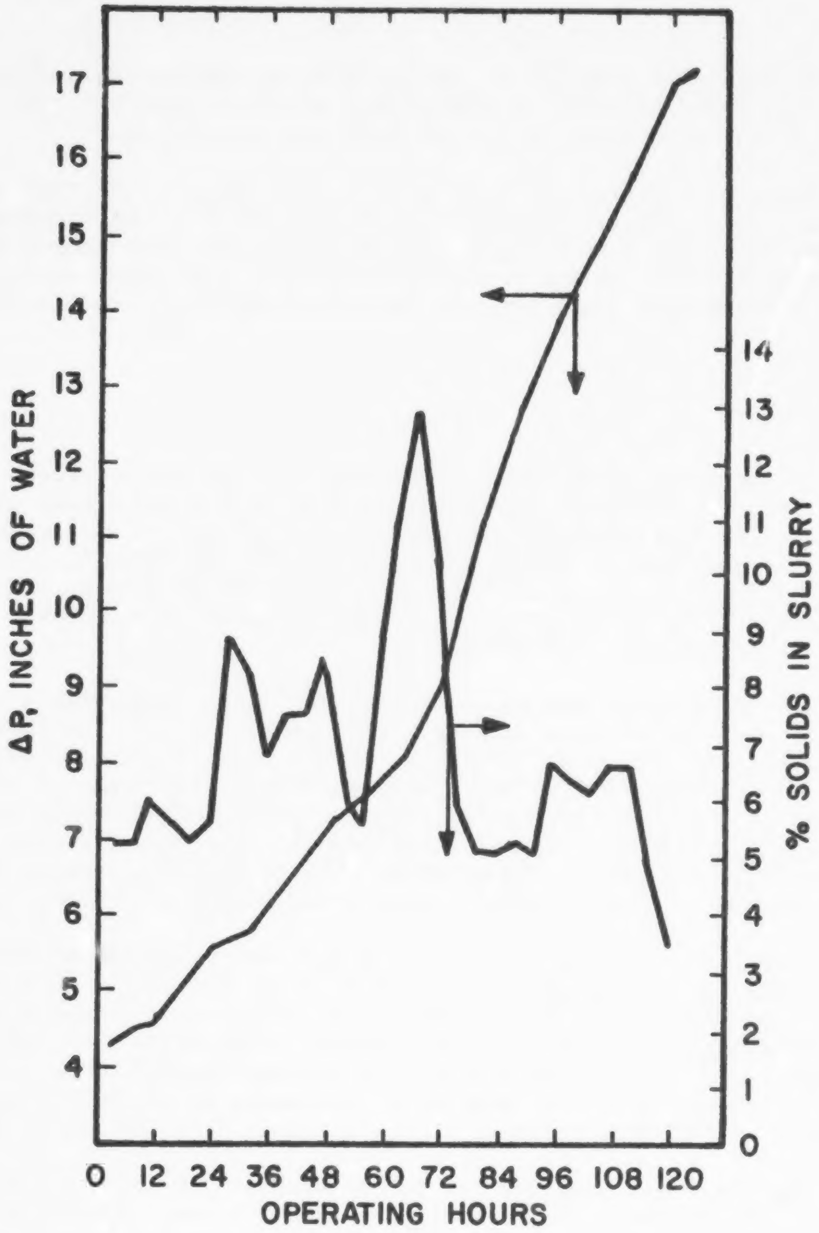

FIGURE 5

Ventri-Rod Crossflow Scrubber Pressure Differential and Slurry Solids Content

Petrographic examination of the scale formed on the packing indicated a bulk phase (70-95%) of $CaSO_4 \cdot 2H_2O$, a minor phase (10-20%) of $CaSO_3 \cdot 0.5H_2O$, and very minor phases of $CaCO_3$ and $CaMg(CO_3)_2$.

These tests indicated that a packed scrubber of the type tested is very prone to plugging, either by solids deposition or by chemical scaling. Although the SO_2 removal efficiency was probably acceptable (about 80% under the conditions tested), it was concluded that such a scrubber should not be selected for the Widows Creek project because operation would likely be unreliable.

Spray Tower

In the spray tower design used (Fig 6), the venturi scrubber was integrated into the scrubber by placing a Ventri-Rod element near the bottom of the tower with the spray pointed upward. The objective was to get more SO_2 removal in the venturi (which was quite low in the venturi - packed scrubber arrangement), by inducing a fountain effect that would give more slurry holdup in the scrubber. The auxiliary pilot plant equipment, i.e., tanks, pumps, and blowers, were essentially unaltered.

The spray tower was 32 in. square and 20 ft tall, with a superficial gas velocity of 5 ft/sec at a total gas flow of 2000 scfm. The Ventri-Rod element, mounted in the inlet end of the 32-in. housing, was irrigated from the bottom side cocurrent with the upward gas flow. Two banks of spray nozzles were located in the open tower at 5-ft intervals above the Ventri-Rod element. A chevron-type entrainment separator was mounted in a horizontal outlet section and equipped with a spray on the upstream side to remove accumulated solids. (A simplified sketch of the overall spray tower assembly is shown in Fig 7).

A set of screening tests (open loop) was run first to check the effects of major operating variables (see Part II of this paper). An extended test run then was made, at conditions indicated to be optimum, to identify any problems associated with extended plant operation. The L/G was 60 gal/Mcf--20 each to the spray banks and the Ventri-Rod unit. Pressure drop, at the gas throughput of 2000 acfm, was about 15 in. H_2O across the venturi and 1 in. through the rest of the scrubber. Stoichiometry was 1.5.

The plant was operated for 354 hr with only a total of 20 hr of downtime for maintenance. SO_2 removal averaged 77% over the entire test (Fig 8). The pronounced decrease in SO_2 removal occurring about 270 hr after startup and lasting about two shifts was caused by poor distribution of slurry in the tower. A large hole was eroded in the bottom spray header, resulting in poor slurry distribution and reduced SO_2 removal.

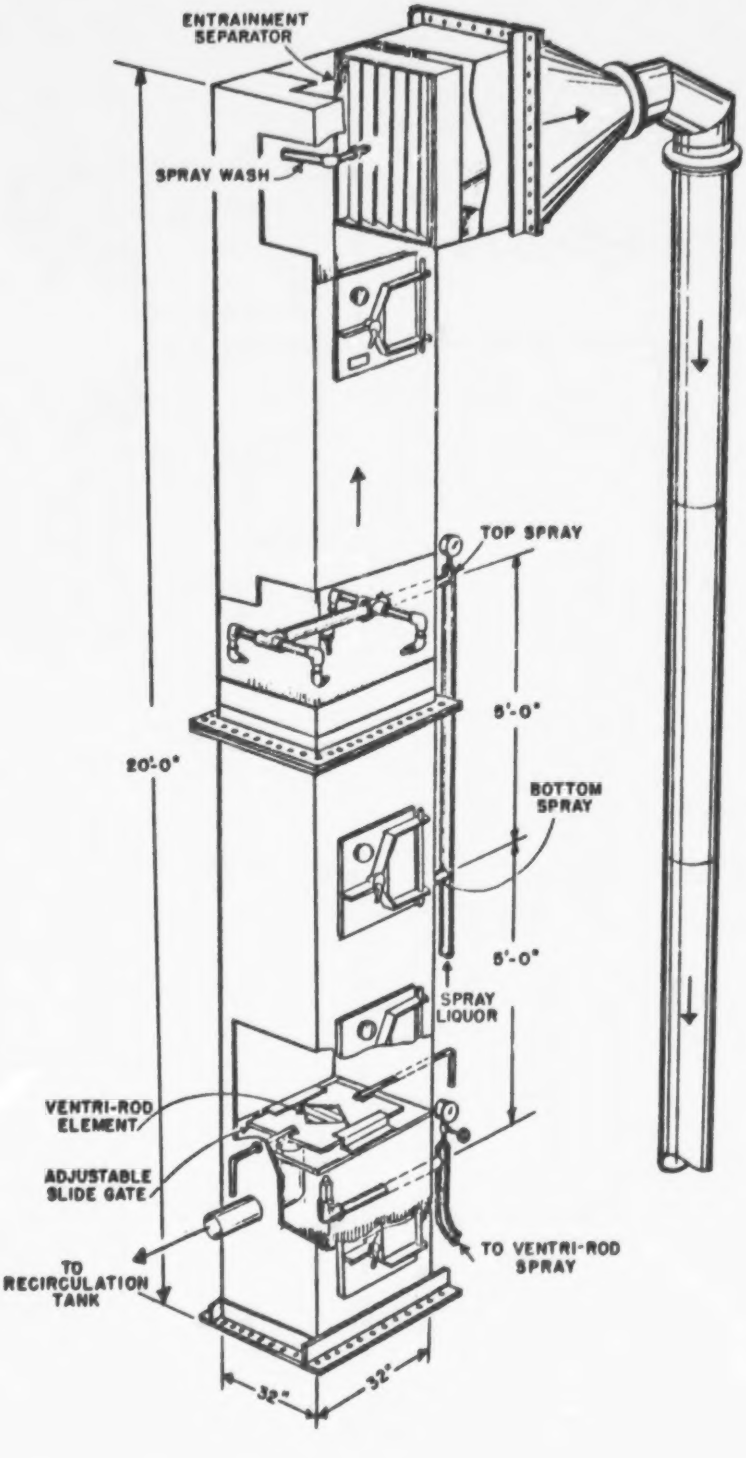

FIGURE 6

Ventri-Rod - Spray Tower

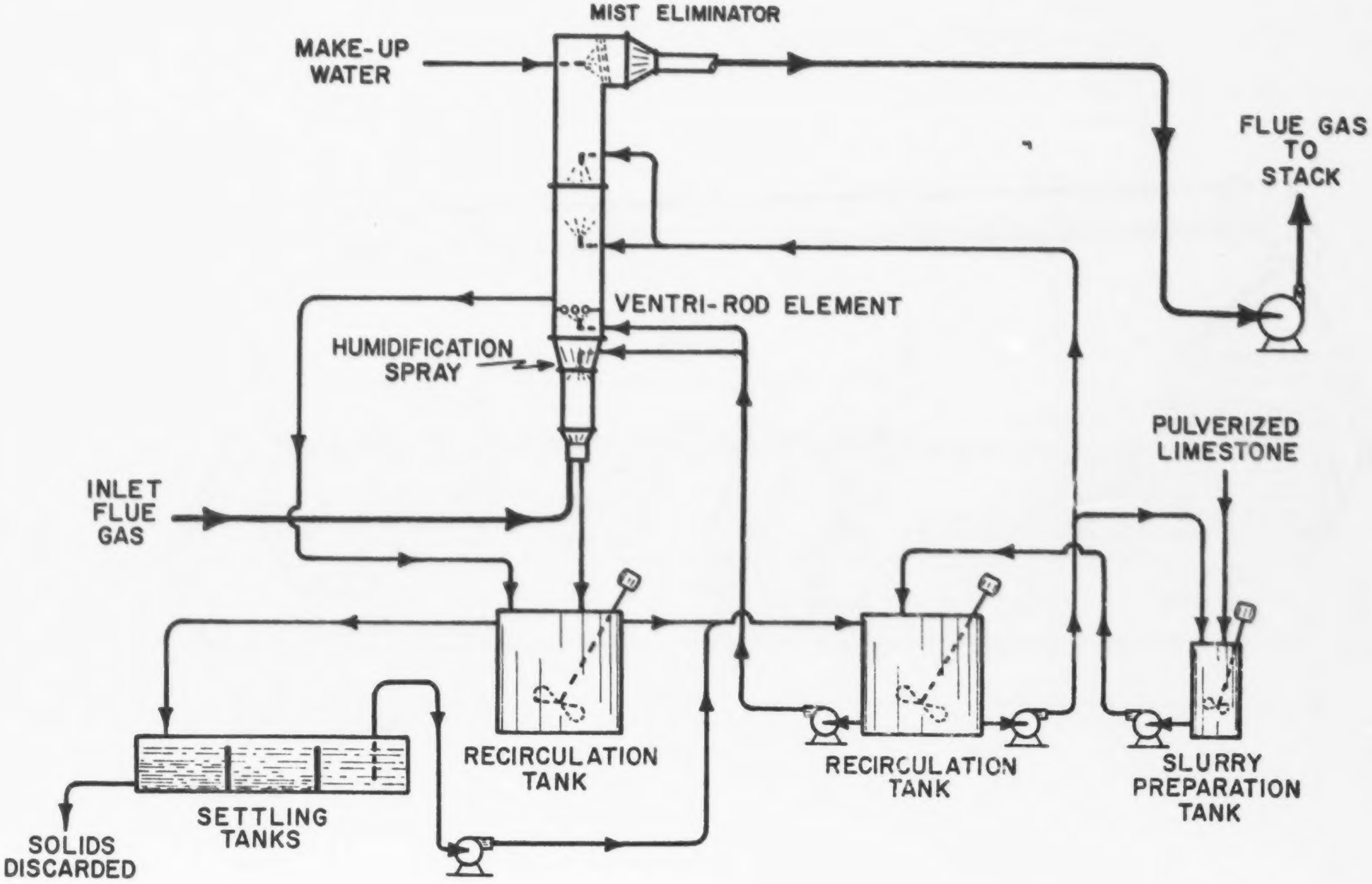

FIGURE 7

Pilot Plant with Ventri-Rod - Spray Tower Scrubber Configuration

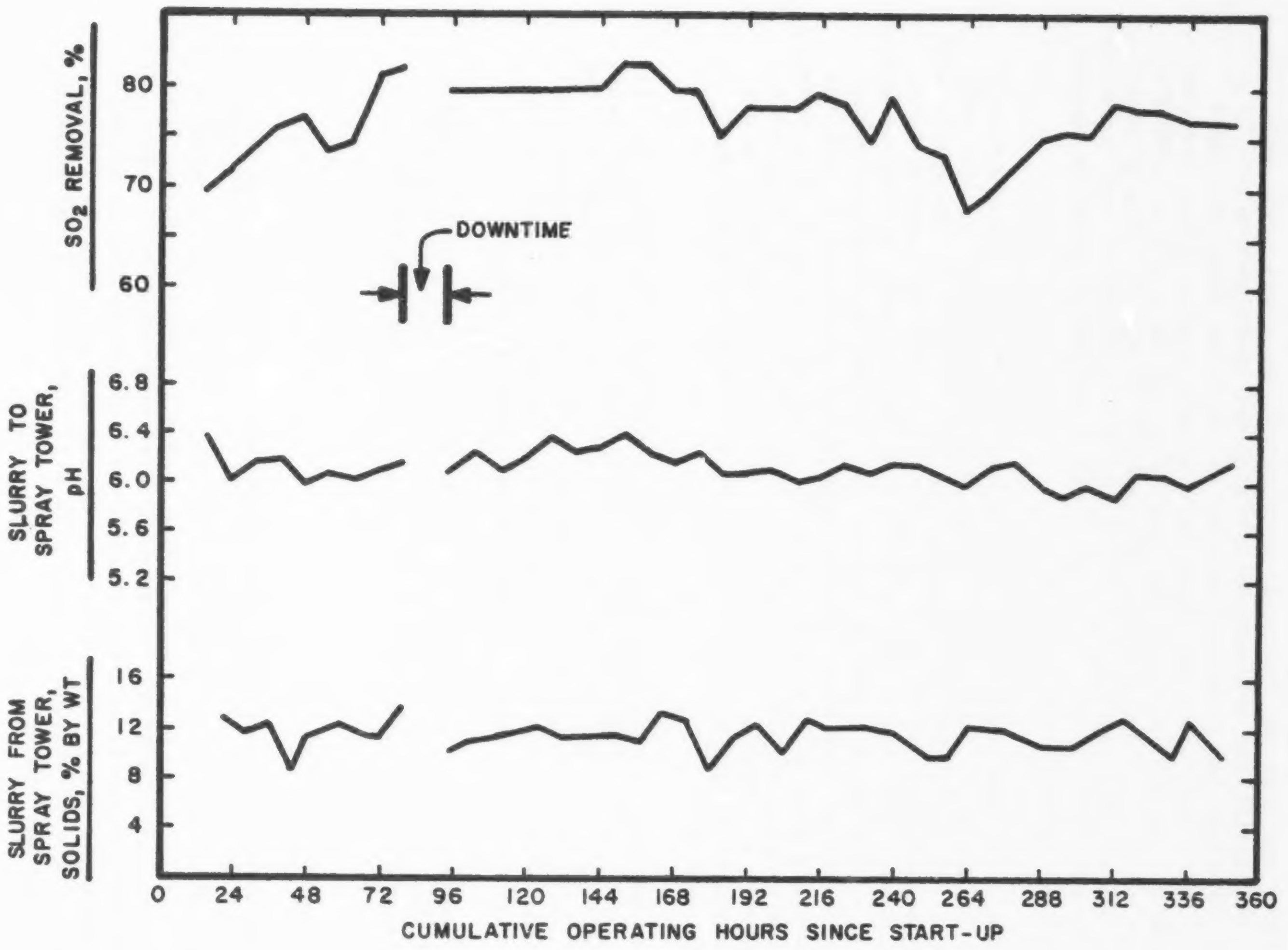

FIGURE 8

SO$_2$ Removal, pH, and Solids Concentration in Spray Tower Recirculation Slurry

After the test was routinely terminated, the spray tower was inspected. No significant scaling had occurred but there were heavy deposits of limestone and reaction products in the tower above the upper spray bank. These soft deposits, which were several inches thick, occurred only in areas not wetted by the sprays; more than 50% of the mist eliminator inlet was sealed off. Although the deposits were heavy, the total pressure drop across the scrubber system, including the mist eliminator, had increased by only 1 in. H_2O--from 16 to 17 in. H_2O. The accumulation could be removed easily with high-velocity jets of water.

There was some indication in this run that better operation would be obtained if the spray banks were raised to a higher level, to give more space between the Ventri-Rod and the upper sprays. Therefore the sprays were raised 5 ft and another set of open-loop screening tests was carried out. (A third spray was also installed in the top of the scrubber to prevent solids accumulation.) The results indicated that the changes improved operation. It was also indicated (see Part II) that higher gas velocities through the scrubber could be used to reduce the scrubber cost and the area requirements by making the cross-sectional area smaller. The previous screening tests had been made at superficial gas velocities of 4.6 to 6.2 ft/sec; the new test series indicated that 7.8 ft/sec might be used without significantly reducing SO_2 removal.

An extended closed-loop run (168 hr) was made, therefore, at (1) 7.8 ft/sec, (2) L/G of 55 gal/Mcf (20 to Ventri-Rod, 5 to first spray bank, 15 to second, and 15 to the new top spray), and (3) 1.5 stoichiometry. The SO_2 removal was only 66%, however, as compared with the 76% predicted from the screening tests and the 78% obtained in the earlier run at 4.6 ft/sec. Possible reasons for the lower removal are discussed in Part II.

These tests indicate that the spray tower is a reliable scrubber for SO_2 removal, but is not as good a contactor as a fixed-bed scrubber. Also, the limitation in gas velocity may be an important cost factor.

Mobile-Bed Scrubber

The mobile-bed scrubber type tested was the Turbulent Contact Absorber (TCA), manufactured by Universal Oil Products Company. It consists of three beds of mobile packing spaced vertically (Fig 9) and is designed to operate at 8-13 ft/sec. Each packing unit consists of a 1-ft static depth of 1.5-in. hollow plastic spheres, retained by wire mesh grids 4 ft apart. The flow of gas through the bed causes the spheres to move rapidly in a random pattern between the two retaining grids. The scrubbing liquor is fed above the top retaining grid through an open-pipe distributor and flows countercurrently to the gas flow.

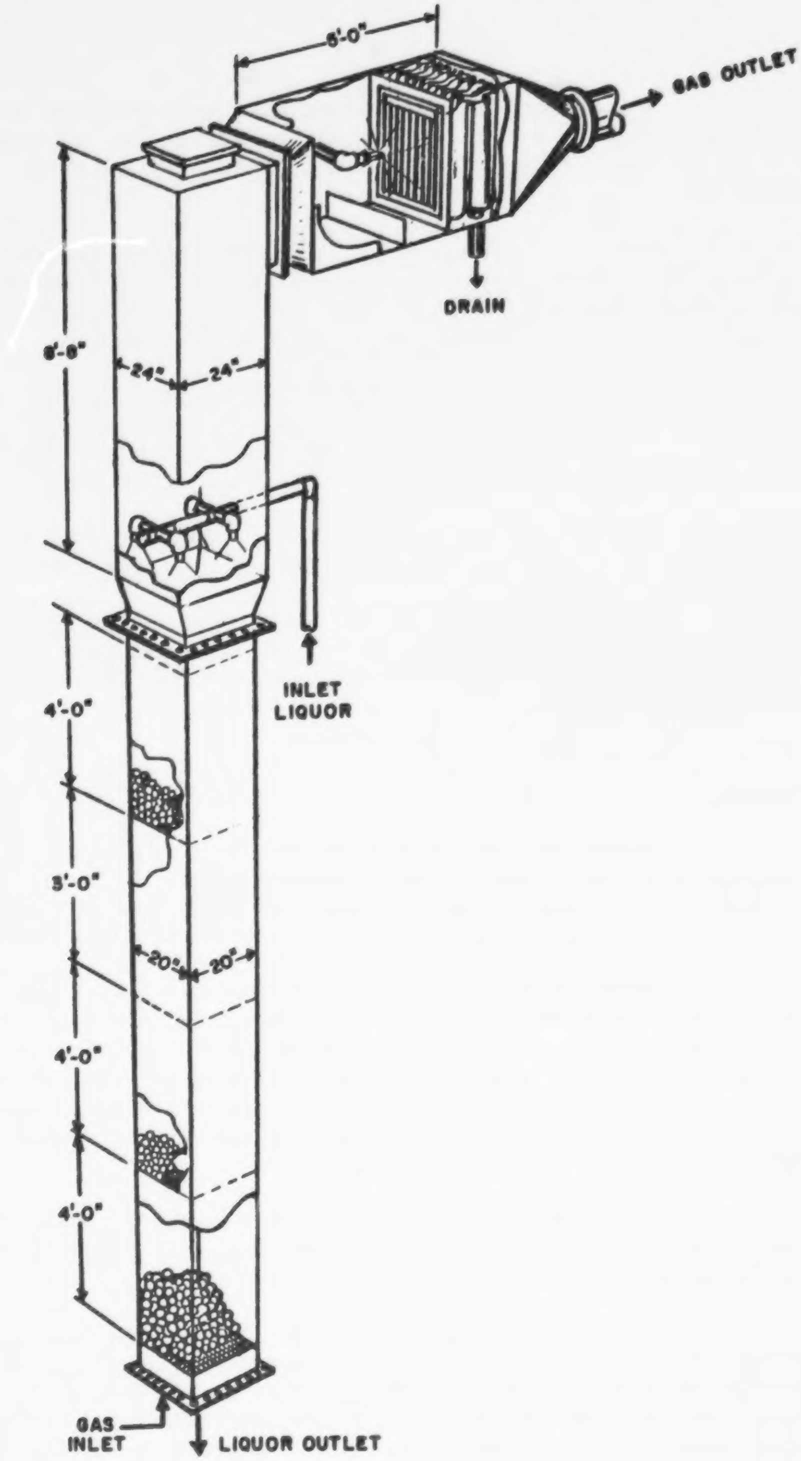

FIGURE 9

Mobile-Bed (TCA) Scrubber

A chevron-type mist eliminator manufactured by the Heil Process Equipment Company was installed in the horizontal housing at the outlet of the scrubber. The pilot plant configuration with the TCA scrubber is shown in Figure 10.

After the usual series of screening tests (Part II), a 172-hr closed-loop run was made at a gas velocity of 12.5 ft/sec, a total L/G of 48 gal/Mcf, and 1.5 stoichiometry. The total pressure drop through the scrubber was 9 in. H_2O during the entire test period.

After routine termination of the run, inspection of the scrubber showed a small accumulation of solids immediately below the bottom retaining grid of the first stage. Otherwise, the scrubber elements were clean with no significant evidence of accumulated solids or scale.

Removal of SO_2 was excellent, averaging about 92%. The main problems were ball wear, erosion of grids, and particulate entrainment.

Further tests of the mobile-bed scrubber are being made. If the indicated resistance to scaling can be verified, and the problems of erosion and particulate carryover solved, the scrubber should be a good candidate for large-scale use.

Erosion

Severe and rapid erosion by the circulating slurry has been a major problem with all three of the scrubber types. For each of three, frequent replacement of pipefittings, valves, and pump components, has been necessary. Other problems have been specific to the particular equipment.

Ventri-Rod: During preliminary tests with the crossflow scrubber assembly, a hole was eroded in the Ventri-Rod housing. A 1/2-in.-thick mild steel wear plate welded over the hole was cut through after about 200 hr of operation. A test panel coated with Urecal (a urethane-based coating) was installed in the housing in the area prone to highest erosion. After 300 hr of operation, the welds supporting the panel were eroded through, but the coating on the panel was undamaged.

Spray Tower: During the tests with the spray tower system, the 303 stainless steel spray nozzles and the mild steel lower spray header had to be replaced at intervals of about 300 hr.

Mobile-Bed Scrubber: In the tests made with the TCA scrubber, the weight loss of the plastic spheres has averaged about 10% in 300 hr of operation. During the same period, the weight loss of the bottom retaining grid was about 30%. In tests now being made, finer limestone (88% through 325 mesh) is being used in an effort to reduce erosion. A small test loop is also being assembled in which test specimens can be studied under conditions more closely controlled than is feasible in the scrubber.

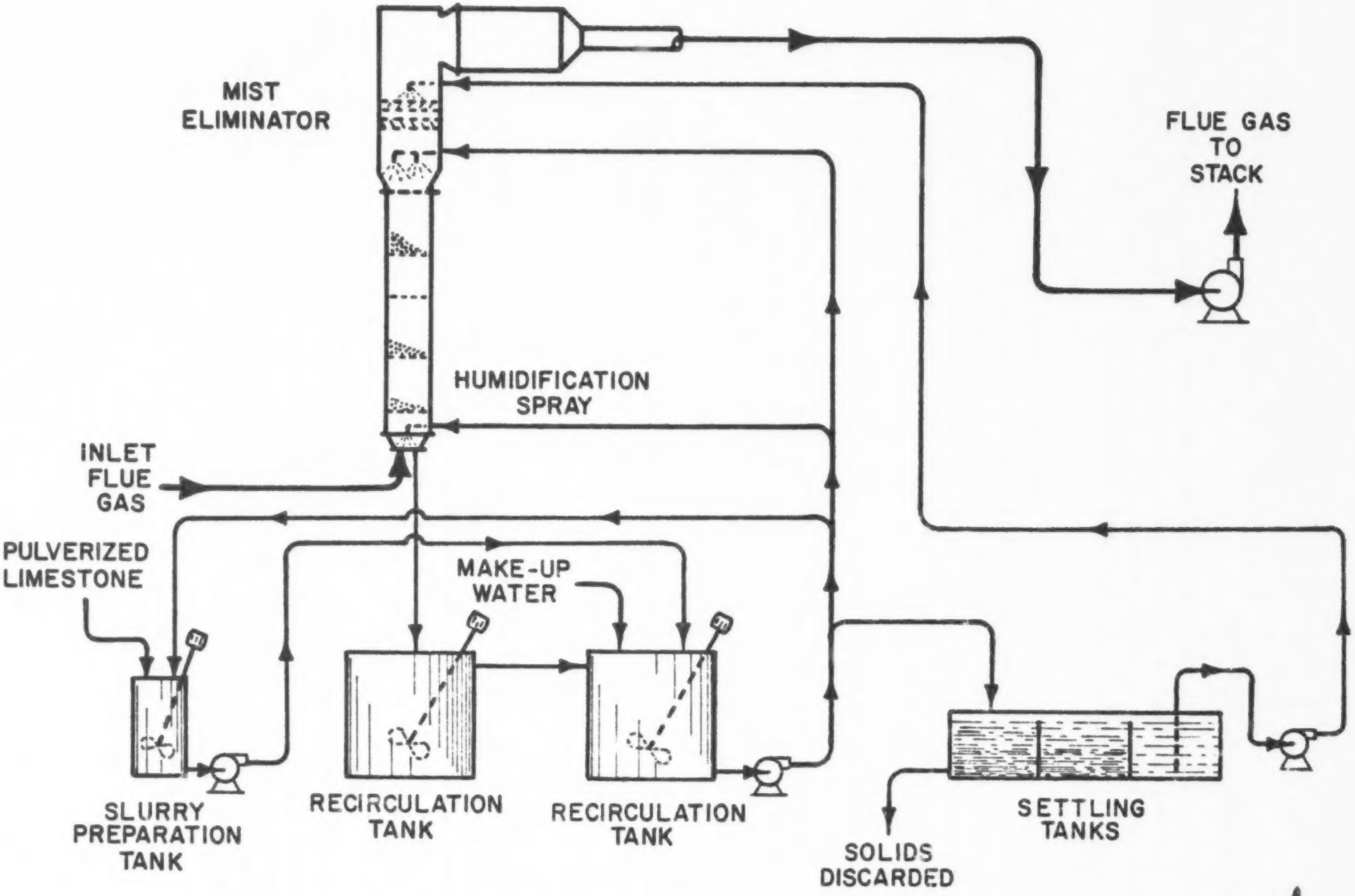

FIGURE 10

Pilot Plant with TCA Scrubber Configuration

Particulate Loading in Exit Gas

The objective in the test program has been to remove fly ash from the gas to the degree that a "clear stack" is obtained. The degree of dust removal required to give a clear stack varies with several conditions, but it seems generally accepted that a level of 0.02 gr/ft^3 (dry) or less is a reasonable objective.

In the TVA pilot plant tests, the particulate loading in the exit gas from the scrubbers tested has averaged about 0.03 gr/scfd from the crossflow, 0.027 and 0.05 gr/scfd from the spray tower (for 4.6 and 7.8 ft/sec gas velocity, respectively) and 0.07 gr from the TCA scrubber (12.5 ft/sec velocity). The particulate loading has been a linear function of the apparent gas velocity in the barrel of the scrubber.

Petrographic analyses of the particles indicate that the material in the exit gas is calcium carbonate or calcium sulfite - sulfate rather than fly ash. Apparently, the fly ash is readily captured and removed in the first stage of each scrubber configuration, even at the low pressure drop in the mobile-bed scrubber (see Part II). The particulate in the exit gas comes from the mist of scrubber slurry that passes the chevron mist eliminator. Tests are currently in progress to develop a more effective mist elimination system.

Tests of scrubber configurations in the pilot plant are continuing. Evaluation of the spray tower and TCA scrubber have not been completed.

Summary

Of the three scrubber types tested, all should give adequate SO_2 removal if properly designed. As to reliability, the fixed bed (crossflow type) is unacceptable because of scaling and plugging. The spray tower and mobile-bed types avoid this problem, but each has other problems that must be solved. The advantages and disadvantages of each, as indicated by the pilot plant work, are listed in Table III.

Further tests are under way to continue evaluation of the spray tower and mobile-bed types. Other scrubber configurations may also be tested. The main remaining problems, on which special studies are planned, are erosion, mist carryover, and slow settling of solids. Ways for avoiding unstable pH at low limestone stoichiometry will also be explored.

TABLE III

Evaluation of Scrubber Types

Spray Tower	Mobile-Bed Scrubber (TCA)
Advantages	**Advantages**
1. No internals for build up of mud or scale	1. Gas velocity of 12.5 ft/sec possible with good SO_2 recovery
2. Infinite turndown	2. Fly ash removal possible in same unit
3. Spray nozzle and distributor replacement only routine maintenance item	3. Slurry distribution may require only open pipes with splash plates
4. Low pressure drop through tower $-\Delta P$-2.0 in. H_2O or less	4. Excellent gas contacting efficiency
Disadvantages	**Disadvantages**
1. Gas velocity limited (however, preliminary indications are that the velocity may be increased significantly without loss of efficiency)	1. Some internals (support grids, etc.) required that could promote solids accumulation
2. Separate fly ash removal system required	2. Turndown limited
3. High velocity (atomizing nozzles) required for slurry distribution, requring high-pressure pumps	3. Bouncing balls and supporting grids must be replaced at regular intervals because of erosion
4. Gas contacting efficiency relatively low	4. Pressure drop across scrubber of 9 in. or more required
	5. Mist elimination problem aggravated by high gas velocity

II. EXPERIMENTAL DESIGN AND DATA ANALYSIS FOR SPRAY AND MOBILE-BED SCRUBBERS

By

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As described in Part I of this paper, three scrubber types have been tested in the TVA pilot plant studies on limestone slurry scrubbing of SO_2. The fixed-packing type was abandoned because of scaling, leaving the spray tower and mobile bed as the candidates for full-scale application. In the tests of each type, short-term tests (open loop) were made to evaluate effects of the major operating parameters and to determine the best combination for extended closed-loop runs aimed at evaluating operational reliability.

The basic experimental plan used for all the screening tests was the $2^N (N = 1, 2, 3, . . .)$ factorial or fractional factorial. At the completion of each test series, the data were analyzed by analysis of variance and regression analysis.

For both scrubber types, preliminary tests indicated that of the several operating parameters, four had the most significant effect:

1. Liquid to gas ratio (L/G)
2. Gas velocity (V)
3. Pressure drop (ΔP)
4. Distribution of slurry between scrubber units

Spray Tower

The first test series consisted of 20 tests with the spray tower as shown in Figure 6 in Part I. This was a 1/2 replicate of a 2^5 factorial experiment, with four center points added. The five variables studied and the range of each variable were as follows:

	Variable	Range
1.	L/G to Ventri-Rod (L/G_{VR}), gal/Mcf	20-40
2.	Pressure drop across Ventri-Rod (ΔP_{VR}), in. H_2O	7-15
3.	L/G to first spray above venturi (L/G_{S1})	0-10
4.	L/G to second spray above venturi (L/G_{S2})	0-10
5.	Gas velocity, cfm ft/sec	2000-2700 4.6-6.2

The other operating conditions are given in Part I. Detailed test data are listed in Table IV.

TABLE IV

Test Conditions and Results from Screening Tests of Spray Tower Scrubbing (First Series)

Test No.	Gas flow, cfm	ΔP_{VR}, in. H_2O	ΔP overall, in. H_2O	L/G, gal/Mcf VR	L/G, gal/Mcf S1	L/G, gal/Mcf S2	% solids	SO_2 removal, % average	Range
1	2700	6.5	10.4	40	0	10	12	64	59-69
2	2000	6.0	-	20	10	0	25	55	53-58
3	2000	14.5	15.0	20	0	0	16	58	57-62
4	2000	15.0	15.6	20	10	10	16	68	
5	2350	10.0	10.6	30	5	5	16	58	54-63
6	2700	13.2	15.9	20	0	10	13	64	
7	2700	13.9	16.9	40	10	10	-	71	70.5-71.4
8	2000	15.6	17.0	40	10	0	12	60	60.0-60.3
9	2000	7.2	8.5	40	10	10	16	59	57-60
10	2350	11.1	12.4	30	5	5	15	59	58-61
11	2700	7.4	8.3	20	10	10	13	60	
12	2000	15.2	16.7	40	0	10	16	61	60-63
13	2700	15.0	17.0	20	10	0	17	60	59-62
14	2000	7.4	8.7	40	0	0	16	53	51-55
15	2350	11.3	12.7	30	5	5	14	56	56-57
16	2700	7.0	8.9	20	0	0	17	50	49-51
17	2000	7.0	8.4	20	0	10	13	59	59
18	2700	15.0	17.0	40	0	0	16	66	66
19	2700	7.2	8.4	40	10	0	20	57	56-59
20	2350	11.6	14.1	30	5	5	18	60	58-61

Although each variable had a statistically significant effect on percent SO_2 removal, the two largest effects were the pressure drop across the venturi and the L/G to the second spray above the venturi. The regression equation derived from the data is as follows:

Predicted % SO_2 removal =

$$59.9 + \frac{17}{16} X_1 + \frac{51}{16} X_2 + \frac{15}{16} X_3 + \frac{47}{16} X_4 + \frac{19}{16} X_5 + \frac{31}{16} X_6 \qquad (1)$$

where

$X_1 = (L/G_{VR} - 30)/10$

$X_2 = (\Delta P_{VR} - 11)/4$

$X_3 = (L/G_{S1} - 5)/5$

$X_4 = (L/G_{S2} - 5)/5$

$X_5 = (\text{Gas velocity} - 2350)/350$

$X_6 = X_1 \cdot X_5$

This equation accounts for 90% of the total variation of the data. The remaining 10% is composed of 3.0% due to curvature (i.e., x_i^2) and 7.0% error. The analysis of variance is tabulated in Table V and the predicted vs observed values are given in Figure 11. Based upon the analysis of the data, 95% of the actual or observed values will be within 3% of the predicted percent SO_2 removal.

Two of the results from this test series were encouraging. First, the contribution to SO_2 removal from the lower spray (S1) was small compared with other variables. Since this spray was located in a position just above the venturi and was subject to severe erosion, removing it would simplify operation without any great loss of SO_2 removal efficiency. Secondly, increase in gas velocity, within the range studied, improved SO_2 removal slightly rather than reducing it.

The SO_2 removal in the extended run made under closed-loop conditions in the venturi - spray tower (Part I) checked with the predicted removal from the open-loop screening tests within experimental error.

The second spray tower test series was run after the spray banks had been raised to a higher level and a wash spray (S3) installed at the top of the scrubber. The series consisted of two blocks of tests composed of a full factorial for two variables (2^2) plus one center point in the first block (Table VI).

TABLE V

Analysis of Variance for Screening Tests of Spray Tower Scrubbing (First Series)[a]

Source	Sum of squares	Degrees of freedom	Mean square[b]	
Mean	71,760.2	1		
L/G_{VR}	18.06	1	18.0625	
ΔP_{VR}	162.56	1	162.5625	
L/G_{S1}	14.06	1	14.0625	
L/G_{S2}	138.06	1	138.0625	
Velocity	22.56	1	22.5625	
$L/G_{VR}\cdot$velocity	60.06	1	60.0625	
Residual	48.42	13		
Lack of fit	39.6750	10		
Curvature	13.6	1		
Interaction	26.0750	9	2.897)	2.9 (pooled estimate)
Error	8.75	3	2.92)	
Total	72,224	20		

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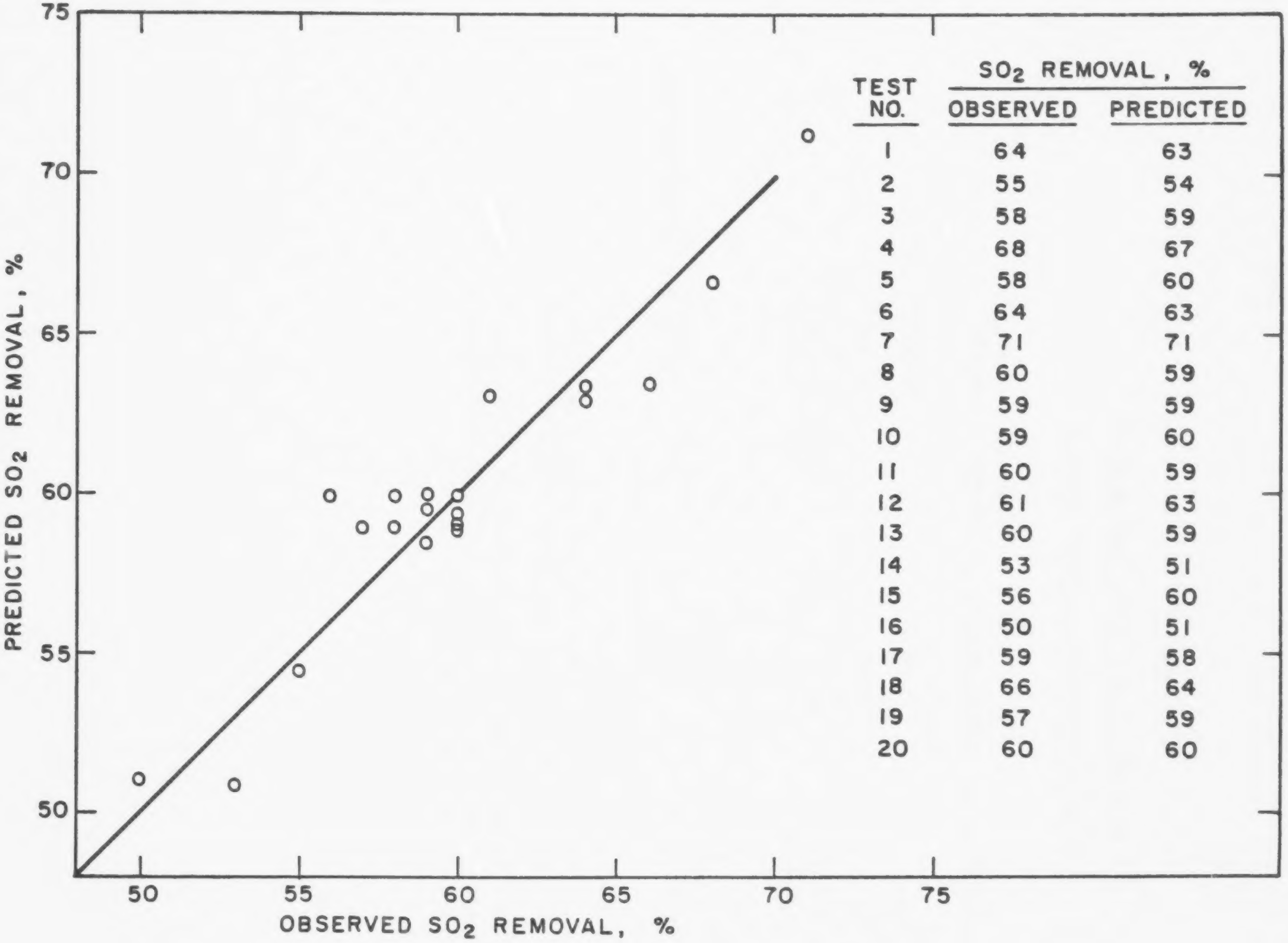
[a] Correlation coefficient = 0.96; index of determination = 0.92

[b] All values significant at $\alpha = 0.01$, where α indicates degree of confidence (i.e., 0.01 indicates 1% possibility of variable not being significant).



TEST NO.	SO_2 REMOVAL, %	
	OBSERVED	PREDICTED
1	64	63
2	55	54
3	58	59
4	68	67
5	58	60
6	64	63
7	71	71
8	60	59
9	59	59
10	59	60
11	60	59
12	61	63
13	60	59
14	53	51
15	56	60
16	50	51
17	59	58
18	66	64
19	57	59
20	60	60

FIGURE 11

Comparison of Predicted and Observed Results in Screening Tests of Spray Tower Scrubbing (First Series)

TABLE VI

Test Conditions and Results from Screening Tests of Spray Tower Scrubbing (Second Series)[a]

Test No.	ΔP_{VR},[b] in. H_2O	ΔP overall, in. H_2O	L/G				% SO_2 removal
			VR[b]	S1	S2	S3	
1	7.3	10.3	20	10	10	10	67.1
2	7.4	10.6	38	10	10	10	71.6
3	15.1	17.9	20	10	10	10	75.9
4	15.2	18.3	38	10	10	10	75.3
5	11.2	14.5	30	10	10	10	70.1
6	15.1	18.0	20	0	18	9	64.3
7	15.0	17.8	20	20	0	10	62.7
8	15.1	18.0	20	0	0	10	58.8
9	15.0	18.2	20	20	17	10	72.8

[a] Gas flow, 2700 cfm (6.2 ft/sec); L/G to humidification spray, 5.5 gal/Mcf.

[b] Ventri-Rod scrubber.

The variables studied and the range of each were as follows:

Variable	Range
1. L/G to Ventri-Rod, gal/Mcf	20-38
2. L/G to S1, gal/Mcf	0-20
3. L/G to S2, gal/Mcf	0-18
4. ΔP across Ventri-Rod, in. H_2O	7-15

All tests were conducted at the maximum system velocity of 2700 ft^3/min (6.2 ft/sec). In the first block of five tests, the ΔP across the venturi and the L/G to the venturi were varied. Analysis of these data resulted in the following equation:

$$\% \ SO_2 \ \text{removal} = 72 + 3\Delta P + L/G - 1.5(L/G)(\Delta P) \qquad (2)$$

$$\text{where} \qquad \Delta P = (\Delta P_{VR} - 11)/4$$

$$L/G = (L/G_{VR} - 29)/9$$

Table VII gives the analysis of variance. The L/G was not significant over the range tested.

TABLE VII

Analysis of Variance for Block 1 of Second Test Series on Spray Tower

Source	Degrees of freedom	Sum of squares	Mean square	F value
Mean	1	25,920		
ΔP	1	36	36	12[a]
L/G	1	4	4	1.3[b]
$(\Delta P)(L/G)$	1	9	9	3[b]
Residual	1	5	5	1.67[b]
Error[c]	(12)		3	
Total	5	25,974		

[a] Significant at $\alpha = 0.01$.
[b] Not significant or significant at $\alpha > 0.10$.
[c] Error variance assumed to be 3.0 with 12 degrees of freedom.

The next block of tests was run with L/G to sprays S1 and S2 varied but with venturi ΔP and L/G held constant. The resulting equation was

$$\% \ SO_2 \text{ removal} = 65 + 3.25L/G_1 + 3.75L/G_2 + 1.25(L/G_1 \cdot L/G_2) \quad (3)$$

where $L/G_1 = (L/G \text{ to S1-10})/10$

$L/G_2 = (L/G \text{ to S2-9})/9$

The analysis of variance is given in Table VIII.[1]

This block indicates that the two sprays are both important in SO_2 removal but are independent and the greater the L/G to each the greater the SO removal. Thus raising the sprays in the scrubber did increase the effectiveness of the lower spray (S1).

---

[1] From previous error estimates, the error variance is estimated to be 3.0 with 12 degrees of freedom (see Table V). This estimate is used as the error throughout the Ventri-Rod - spray tower test work.

TABLE VIII

Analysis of Variance for Block 2 of Second Test Series on Spray Tower[a]

Source	Degrees of freedom	Sum of squares	Mean square	F value
Mean	1	16,770.25		
L/G_1	1	42.25	42.25	14.08[b]
L/G_2	1	56.25	56.25	18.75[b]
$L/G_1 \cdot L/G_2$	1	6.25	6.25	2.08[c]
Total	4	16,875.00		

---

[a] Error variance assumed to be 3.0 with 12 degrees freedom.

[b] Significant at $\alpha = 0.01$.

[c] Not significant or significant at $\alpha > 0.10$

A third series of tests (Table IX) were run to test the system at the maximum velocity attainable, 3400 ft^3/min (7.8 ft/sec). This group consisted of a 1/2 replicate of a 2^5 factorial experiment with 4 center points added for a total of 20 tests. Again, open-loop conditions were used. Analysis of the test results gave the equation:

$$\% \; SO_2 \text{ removal} = 68.9 + 0.82L/G_{VR} + 0.96L/G_1 + 2.38L/G_2 + 1.03\Delta P_{VR}$$
$$- 1.55(L/G_{VR})(L/G_3) + 0.95(L/G_{VR})(\Delta P_{VR}) - 1.93(L/G_1)(L/G_2)$$
$$- 0.85(L/G_2)(L/G_3) + 2.2(L/G_2)(\Delta P_{VR}) + 1.63(L/G_3)(\Delta P_{VR}) \qquad (4)$$

where

L/G_{VR} = (L/G to Ventri-Rod-28)/7

L/G_1 = (L/G to S1-10)/5

L/G_2 = (L/G to S2-10)/5

L/G_3 = (L/G to S3-10)/5

ΔP_{VR} = (ΔP to Ventri-Rod-12)/3

Each of the variables in the above equation is significant at $\alpha = 0.2$ or lower. The analysis of variance is given in Table X, along with the t - statistic for each variable.

TABLE IX

Test Conditions and Results from Screening Tests of Spray Tower Scrubbing (Third Series)[a]

Test No.	ΔP, in. H_2O		L/G				% SO_2 removal
	VR	Overall	VR	S1	S2	S3	
1	14.5	19.8	20	5	15	15	76.8
2	9	19.1	35	15	5	15	68.9
3	15	21.6	20	15	5	15	70.4
4	15	23.1	35	5	15	5	77.6
5	12	21.5	28	10	10	10	77.3
6	8.9	22.0	35	5	5	5	65.8
7	15.1	23.0	35	15	5	5	68.2
8	15.1	23.1	35	5	5	15	64.3
9	13.3	22.6	20	15	15	15	71.3
10	13.5	23.2	28	10	10	10	68.7
11	9.0	24.5	20	15	5	5	68.9
12	15.0	1.8[b]	20	15	15	5	68.3
13	14.9	2.1[b]	35	15	15	15	75.6
14	9.2	2.0[b]	35	15	15	5	70.7
15	12.6	20.5	28	10	10	10	70.4
16	11.8	24.5	20	5	5	15	65.7
17	11.0	21.5	35	5	15	15	67.1
18	15.0	20.5	20	5	5	5	57.0
19	13.0	25.9	20	5	15	5	70.1
20	12.1	20.6	28	10	10	10	69.5

---

[a] Gas flow, 3400 cfm (6.8 ft/sec); L/G to humidification spray, 4.4 gal/Mcf.

[b] Inch Hg.

TABLE X

Analysis of Variance for Third Test Series on Spray Tower[a]

Source	Degrees of freedom	Sum of squares	Mean square	F ratio
Regression	10	367.73	36.67	14.65[b]
Error	9	22.59	2.51	
Total	19	390.32		

Variable	t - statistic	Variable	t - statistic
L/G to VR	1.73	$(L/G_1)(L/G_2)$	-4.58
L/G to S1	2.40	$(L/G_2)(L/G_3)$	-2.08
L/G to S2	5.30	$(L/G_2)(\Delta P)$	4.31
ΔP to VR	1.78	$(L/G_3)(\Delta P)$	3.21
$(L/G_{VR})(L/G_3)$	-3.69		
$(L/G_{VR})(\Delta P)$	1.71		

---

[a] Correlation coefficient = 0.97; index of determination = 0.94.

[b] Significant at $\alpha = 0.01$.

The most significant variables in the third series are pressure drop across the venturi and the L/G to the upper spray, S2. These tests indicate that although increasing the velocity above 2700 ft^3/min (6.2 ft/sec) does reduce the SO_2 removal, this effect can be offset by judicious choice of slurry distribution. The following tabulation illustrates the effect of velocity on SO_2 removal when the slurry distribution to the sprays is held constant.

Velocity, ft/sec	ΔP_{VR}, in. H_2O	L/G, gal/Mcf VR	S1	S2	S3	SO_2 removal, %
4.6	15	20	10	10	10	72
6.2	15	20	10	10	10	76
7.8	15	20	10	10	10	68
4.6	15	30	10	10	10	72
6.2	15	30	10	10	10	75
7.8	15	30	10	10	10	71
4.6	15	38	10	10	10	72
6.2	15	38	10	10	10	75
7.8	15	38	10	10	10	72

Under these conditions, 2700 cfm gives the maximum removal. By varying the distribution to the sprays, however, good results can be obtained at 3400 cfm--as shown in the following tabulation.

Velocity, ft/sec[a]	ΔP_{VR}, in. H_2O	L/G, gal/Mcf VR	S1	S2	S3	SO_2 removal, %
7-8	9	35	5	15	5	73
7-8	9	20	15	5	10	70
7-8	15	20	5	15	15	76
7-8	15	20	5	15	10	74
7-8	15	35	15	15	15	78

[a] 3400 cfm.

In view of these results, an extended closed-loop run (165 hr) was made at 3400 cfm, 15 ΔP_{VR}, 20L/G_{VR}, 5L/G_{S1}, 15L/G_{S2}, and 15L/G_{S3}. The average removal, however, was only 66% as compared with the predicted 76%. The cause of this is unknown; the removal was about 70% at the end of the run (stopped to install a different type of scrubber), and perhaps would have improved further if time had been available for extending the run.

Mobile-Bed Scrubber

In screening tests with the mobile-bed (TCA) scrubber, the variables were gas velocity, L/G to the main slurry inlet (S1) over the mobile beds, and L/G to the wash spray (S2) in the top of the scrubber. Test conditions and results for the 16 tests are given in Table XI. In developing the equation, test 5 was not included and tests 11 and 16 were averaged to give a total of 14 tests. The equation derived is as follows:[1]

$$\% \ SO_2 \text{ removal} = 64.58 + 5.04L/G_2 + 0.855V \cdot L/G_1 - 0.941(L/G_1)(L/G_2) \qquad (5)$$

where V = velocity (cfm)/100, L/G_1 = (L/G to S1)/10,

and L/G_2 = (L/G to S2)/10

The analysis of variance and t - statistics are given in Table XII. The t - statistics for each variable are significant at $\alpha = 0.05$ or lower.

---

[1] It should be remembered that all regression equations strictly apply only within the experimental region and that extrapolation can be hazardous. This is particularly evident in the TCA system as it is very easy to flood the beds at certain conditions and in fact too large an L/G may be detrimental.

TABLE XI

Test Conditions and Results for Screening Tests on Mobile-Bed Scrubber[a]

Test No.	Gas flow, ft/sec	ΔP through scrubber, in. H_2O	L/G, gal/Mcf		% SO_2 removal
			S1	S2	
1	10.5	7.1	12	29	81
2	16.2	16.5	4	10	77
3	16.2	19.6	12	16	82
4	10.5	5.6	12	17	71
5	16.2	24.0	32	15	74
6	10.5	9.0	52	29	95
7	16.2	16.7	4	16	76
8	10.5	9.0	52	17	95
9	16.2	18.6	12	10	79
10	14.4	22.0	35	16	94
11	13.3	7.7	20	17	84
12	8.3	6.1	15	36	86
13	8.3	5.4	15	21	79
14	8.3	8.5	65	36	89
15	8.3	7.7	65	21	86
16	13.3	7.2	20	17	77

[a] L/G to humidification, 15 gal/Mcf.

It is interesting to note that velocity was not a significant independent variable in these tests. It will appear if the level of significance is selected at $\alpha = 0.25$, but the coefficient is positive indicating that increase in velocity will increase SO_2 removal.

At the conclusion of this series, an extended closed-loop run (172 hr) was carried out at conditions selected on the basis of the screening tests (12.5 ft/sec, 34 L/G to main slurry inlet, and 14 L/G to the upper wash spray). Average removal was 92%, close to that predicted.

TABLE XII

Analysis of Variance for Screening Tests on Mobile-Bed Scrubber[a]

Source	Degrees of freedom	Sum of squares	Mean square	F ratio
Regression	3	621.18	207.06	19.5[b]
Error (residual)	10	106.04	10.6	
Total	13	727.22		

Variable	t - statistic
L/G_2	2.9103
(Velocity)(L/G_2)	5.4241
$(L/G_1)(L/G_2)$	-2.6095

---

[a] Correlation coefficient = 0.92
[b] Significant at $\alpha = 0.01$.

Particulate Removal

Since removal of particulate matter as well as SO_2 is required in wet scrubbing with limestone slurry, small-scale tests were made to determine the pressure drop necessary for good removal. This study was conducted at the Widows Creek plant in order to have the same type of dust as in the later full-scale scrubbers; no limestone was involved.

The equipment used to determine required pressure drop was the "Dust Difficulty Determinator," a small orifice-type test scrubber (with a following mobile bed) manufactured by Environeering, Inc. Composition of the coal burned during the test period is given in Table XIII, particle size of the ash in Table XIV, and results of the tests in Table XV.

Data analysis was performed on tests 16 through 22, 24 through 26, 29 through 42, and 45. The first 15 were preliminary, obtained during the shakedown period; the others were rejected because equipment difficulties were believed to have made the results atypical.

TABLE XIII

Composition of Coal Burned During Dust Removal Tests at Widows Creek

Sample	Total moisture, %	Weight percent, dry basis			
		Volatile matter	Ash	Fixed carbon	Sulfur
1	6.6	28.4	20.7	50.9	1.1
2	5.7	31.5	21.0	47.5	2.9
3	5.6	38.2	17.4	44.4	4.1
4	7.4	31.0	18.3	50.7	2.5
5	7.0	31.2	18.1	50.7	3.4
6	7.7	32.2	19.1	48.7	3.1

The analysis indicated that both L/G and ΔP affect the degree of dust removal. The following equation was developed:

$$Y = 0.12\left(\frac{L}{G} \cdot \Delta P\right)^{-0.54} \qquad (6)$$

where

Y = outlet grain loading, gr/ft^3

L = liquid pumping rate, gal/min

G = gas rate, acfm x 10^{-3}

ΔP = pressure drop, in. H_2O

If the pressure drop across a venturi is defined as

$$\Delta P = \frac{L}{G} \cdot V^{1.87} \qquad (7)$$

where V is gas velocity (ft/min),

then substituting equation 7 in 6 gives

$$Y = \frac{0.12G^{0.54}}{L^{0.54}} \Bigg/ \left[\frac{(L)}{(G)} \cdot (V)^{1.87}\right]^{0.54} = \frac{0.12G^{1.08}}{L^{1.08}V^{1.01}} \qquad (8)$$

TABLE XIV

Bahco Particle Size Analysis of Fly Ash During Widows Creek Tests

Test No.	1	2	3	31	32	33	34	35	36	1
Micron size	Inlet (6-28-71) % less than			Inlet (6-29-71) % less than			Inlet (6-30-71) % less than			Outlet (6-28-71) % less than
3.3	3.1	4.6	2.7	3.8	5.4	6.2	4.3	3.5	4.2	1.4
6.5	13.0	20.7	14.0	17.0	19.5	31.8	20.7	18.4	20.6	9.5
9.6	27.6	42.5	31.8	36.0	37.1	49.7	42.9	41.3	40.8	22.2
13.2	48.2	57.1	50.6	59.6	47.7	62.9	60.0	63.7	51.7	35.0
18.0	69.5	64.3	65.7	78.6	54.0	70.2	69.2	79.9	56.1	48.4
23.9	85.0	69.5	79.4	89.6	63.6	74.5	77.7	87.7	54.3	65.6
29.3	89.0	72.7	83.8	92.3	70.3	77.1	81.3	89.7	66.0	71.8
32.4	90.3	74.3	85.4	93.1	73.5	78.6	82.8	90.4	68.6	76.3
74	94.6	86.7	92.4	94.6	86.1	87.5	88.9	91.6	84.5	91.6 (Filter No. 702)

TABLE XV

Dust Removal from Power Plant Stack Gas (Widows Creek Tests)[a]

Run No.	ΔP_{LS} in. H_2O	ΔP_{HS} in. H_2O	ΔP_T in. H_2O	L/G, gal/Mcf			Inlet loading, gr/scfd	Outlet loading, gr/scfd
				LS	HS	T		
1	-	33	33	20	34	54	1.20	0.0068
2	-	11	11	20	19	39	2.00	0.0097
3	-	20	20	24	17	41	5.40	0.027
4	3.6	10	13.6	17	22	39	2.70	0.12
5	3.9	28	31.9	17	22	39	0.62	0.014
6	4.0	11	15	19	14	33	2.30	0.10
7	6.5	11	17.5	7.4	15	22.4	2.00	0.16
8	3.1	21	24.1	18	15	33	2.00	0.027
9	-	46	46	18	15	33	0.34	0.0032
10	0.8	10.4	11.2	20	15.1	35.1	1.68	0.006
11	1.6	21.4	23	19	14.2	33.2	1.40	0.010
12	3.0	32	35	18	14.0	32	1.57	0.010
13	3.0	5	8	20	16	36	4.0	0.007
14	4.0	10.3	14.3	24	14	38	3.0	0.006
15	4.9	15	19.9	13	14	27	2.8	0.006
16	4.0	-	4.0	27	-	27	5.9	0.011
17	2.2	-	2.2	27.7	-	27.7	3.2	0.009
18	1.8	-	1.8	28.3	-	28.3	2.9	0.009
19	2.1	-	2.1	20.2	-	20.2	2.7	0.025
20	2.1	-	2.1	17.5	-	17.5	2.9	0.007
21	2.1	-	2.1	12.8	-	12.8	3.0	0.031
22	-	5.5	5.5	-	15.2	15.2	1.9	0.006
23	-	10.9	10.9	-	10.0	10.0	4.5	0.068
24	-	4.9	4.9	-	7.2	7.2	5.9	0.016
25	-	3.4	3.4	-	5.0	5.0	6.01	0.013
26	-	4.3	4.3	-	7.2	7.2	4.53	0.018
27	-	4.4	4.4	-	10.0	10.0	3.59	0.031
28	0.2	-	0.2	2.6	-	2.6	6.2	2.7
29	0.2	-	0.2	3.9	-	3.9	2.2	0.11
30	0.2	-	0.2	5.2	-	5.2	3.9	0.09
31	1.2	-	1.2	5.2	-	5.2	6.6	0.04
32	0.8	-	0.8	3.9	-	3.9	4.0	0.044
33	0.4	-	0.4	2.6	-	2.6	3.7	0.13
34	1.7	-	1.7	2.6	-	2.6	3.4	0.075
35	3.2	-	3.2	5.2	-	5.2	3.5	0.028
36	3.2	-	3.2	7.8	-	7.8	2.7	0.042
37	2	-	2	4.7	-	4.7	2.4	0.064
38	2	-	2	9.4	-	9.4	3.7	0.038
39	2	-	2	13	-	13	3.3	0.026
40	-	4.9	4.9	-	7.6	7.6	2.2	0.02
41	-	4.5	4.5	-	5.4	5.4	-	0.0246
42	-	4.2	4.2	-	2.1	2.1	5.2	0.0445
43	-	8.8	8.8	-	5.1	5.1	5.5	0.0743
44	-	10.1	10.1	-	4.0	4.0	5.2	0.0483
45	-	10.1	10.1	-	3.0	3.0	4.4	0.03

---

[a] HS = orifice section of scrubber.
LS = mobile-bed section of scrubber.
T = total.

Now let G = ρAV, where A is the cross-sectional area.

Substituting G = ρAV in equation 8 and approximating coefficients,

$$Y = 0.12\left[\frac{A}{L}\right]\rho \qquad (9)$$

Thus the outlet grain loading is a function of the cross-sectional area and the resistance (i.e., L where L = liquid pumping rate) across the area. The analysis of variance, for equation 6 as the regression model, is given in Table XVI.

TABLE XVI

Analysis of Variance for Dust Removal Tests

Source	Sum of squares	Degrees of freedom	Mean square	F
Mean	362.52	1		
Regression	191.97	1	191.97	75[a]
Residual	62.29	23	2.56	
Total	616.78	25		

($R^2 = 0.755$; $R = 0.87$)

---

[a] Significant at $\alpha = 0.01$.

To confirm the model (equation 6), data supplied by the Western Precipitation Corporation from tests on various venturi scrubbers in the western United States were compared with the Widows Creek data (Fig 12). Good agreement was obtained.

In sampling at the Colbert pilot plant, the particulate in the gas from the scrubber has been found to be mainly calcium salts picked up in the scrubber (see Part I). The grain loading attributable to fly ash (based mainly on petrographic examination of the total particulate and estimation of the fly ash percentage) has been less than 0.02 gr/scfd. Correlation with the Widows Creek model is shown in Table XVII. Agreement was fairly good, considering the observed values for fly ash were estimated.

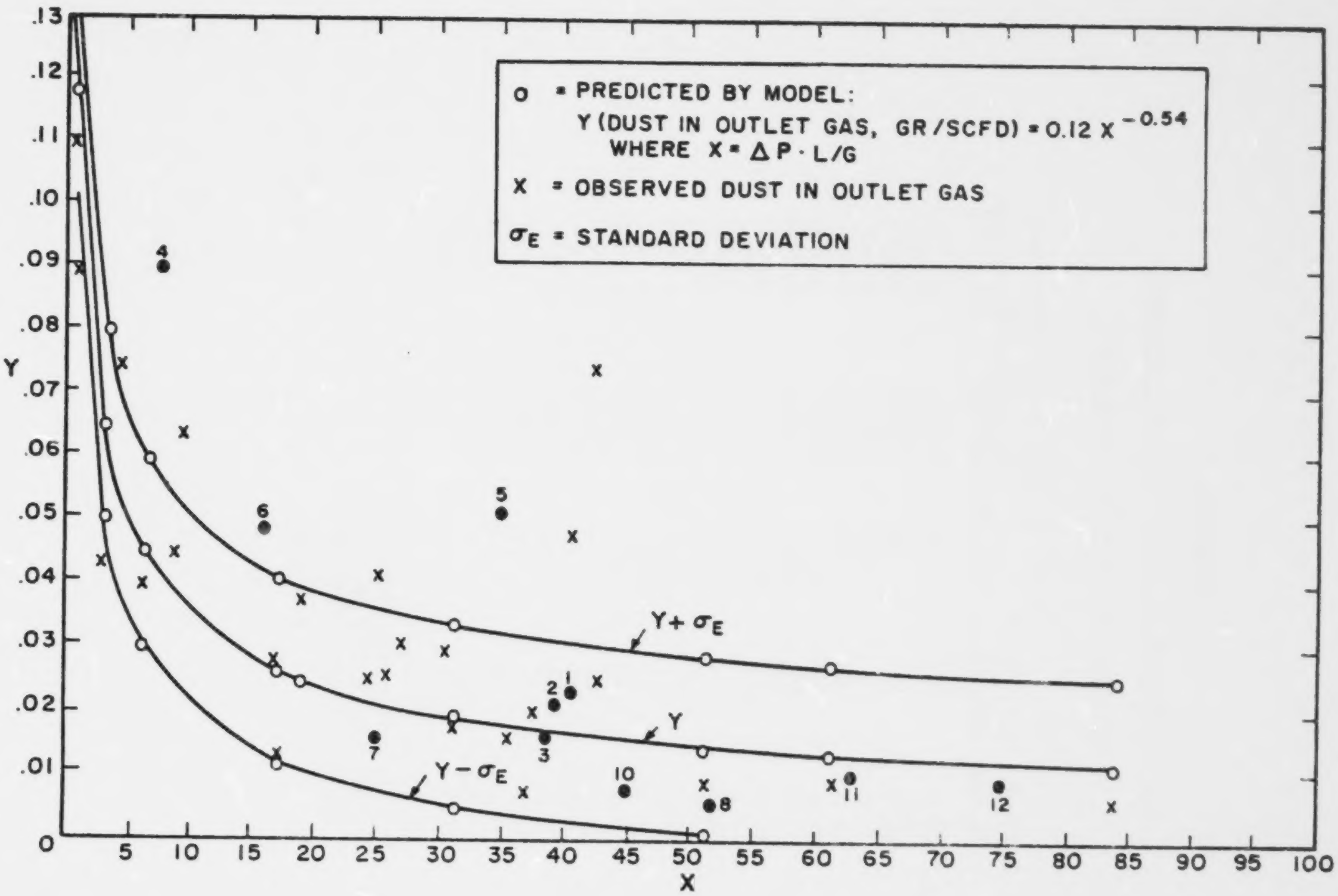


FIGURE 12

Correlation of Observed and Predicted Dust Removal Data from Widows Creek Tests

Data from the Western Precipitation Corporation have been added (denoted by No. 1-12)

TABLE XVII

Fly Ash Removal in Pilot Plant Spray Scrubber: Correlation with Widows Creek Model

ΔP_{VR}[a] in. H_2O	Total L/G,[b] gal/Mcf	$L/G \cdot \Delta P$	Fly ash in outlet gas, gr/scfd	
			Observed	Predicted[c]
6.5	56	364	0.0104	0.0050
6.0	38	228	0.0093	0.0063
14.5	28	406	0.0063	0.0047
15.0	48	720	0.0040	0.0034
10.0	46	460	0.0047	0.0044
13.2	36	475.2	0.0033	0.0043
13.9	66	917.4	0.0037	0.0030
15.6	58	904.8	0.0138	0.0031
7.2	68	489.6	0.0048	0.0042
11.1	46	510.6	0.0031	0.0041
7.4	46	340.4	0.0041	0.0051
15.2	58	881.6	0.0059	0.0031
15.0	36	540.0	0.0030	0.0040
7.4	48	355.2	0.0027	0.0050
11.3	46	519.8	0.0042	0.0041
7.0	26	182	0.0028	0.0072
7.0	38	266	0.0032	0.0059
15.0	46	690	0.0023	0.0035
7.2	56	403.2	0.0027	0.0047
11.6	46	533.6	0.0012	0.0041
15.1	68	1026.8	0.0016	0.0028

---

[a] Pressure drop in Ventri-Rod scrubber.

[b] Total slurry flow to venturi and spray tower.

[c] Based on Widows Creek model:

$$Y \text{ (outlet loading, gr/scfm)} = 0.12\, X^{-0.54}$$

$$\text{where } X = L/G \cdot \Delta P$$

SULPHUR DIOXIDE REMOVAL BY LIMESTONE SLURRY IN A SPRAY TOWER

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SULPHUR DIOXIDE REMOVAL BY LIMESTONE SLURRY IN A SPRAY TOWER

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ABSTRACT

A 4000-cfm pilot plant for removing sulphur dioxide from power plant flue gases has been operated for one year. The sulphur dioxide was removed by contacting flue gas from a coal-fired boiler with a limestone slurry containing 12 per cent by weight of solids in water in a spray tower. Automatic control was used to maintain the pH of the slurry between 5.6 and 6.0. A spray tower was selected because of its simplicity of operation, and because it has a minimum of solid surfaces for scale accumulation. The variables studied included shell velocity, liquid to gas ratio, pressure at the spray nozzles and the slurry retention time. The main variables affecting the sulphur dioxide removal efficiency were gas velocity and liquid to gas ratio. During a continuous 1000-hour run, deposits that formed on the gas inlet duct and on the demister were removed by water jets. The results indicate that a spray tower can be operated with a high degree of reliability and that a sulphur dioxide removal efficiency between 70 to 80 per cent can be achieved using from 20 to 30 per cent above the stoichiometric amount of limestone.

INTRODUCTION

Ontario Hydro, like most North American utilities, is faced with the problem of finding ways to control pollutant emissions from fossil-fuel power plants. Considerable research and development work is being directed toward finding a process to control sulphur oxides emissions and the limestone slurry process has been selected as the most promising for immediate development. This process is being studied in a 4000-cfm pilot plant which draws flue gases from a 300-MW coal-fired boiler, after the electrostatic precipitator. This paper describes the results of recent pilot plant studies.

The sorption of sulphur dioxide by aqueous limestone slurry constitutes a three-phase system, namely, gas, liquid and solid. When sulphur dioxide is transferred into the liquid phase, hydrogen and sulphite ions are formed. Calcium carbonate is also transferred to the liquid phase where it is partially ionized to form calcium and carbonate ions. The calcium and sulphite ions combine chemically to form sparingly soluble calcium sulphite which crystallizes as a separate solid phase. Oxygen in the flue gas is transferred into the liquid together with the sulphur dioxide and partially oxidizes the sulphite resulting in the formation of calcium sulphate, which also crystallizes because of its low solubility. In the presence of a high concentration of sulphite ions in solution, the sparingly soluble calcium sulphite is converted to the more soluble calcium bisulphite. The equilibrium between sulphite and bisulphite ions is reversible and pH controlled.

The transfer of sulphur dioxide is believed to be controlled by the slow rate at which calcium carbonate dissolves. To overcome this limitation, the slurry contacted with a unit volume of gas must contain calcium carbonate substantially in excess of the stoichiometric requirement. With a given per cent solids in the slurry, this can be accomplished by having either a large liquid hold-up in the scrubber or by having a large liquid to gas ratio. The former approach is less desirable because it not only increases the pressure drop across the scrubber but can also lead to the formation of highly supersaturated solutions of calcium sulphate and sulphite with the consequent formation of hard scale over the scrubber surfaces. It therefore appears more desirable to achieve the desired rate of mass transfer by using a high liquid to gas ratio and a spray tower is particularly suitable for this.

Reliability is the key factor affected when a scrubber plugs due to the deposition of solids. Plugging by solids can occur in two ways, namely, by settling of solids in parts of the equipment where the slurry is relatively stagnant, or by the crystallization of dissolved salts from supersaturated solutions on internal surfaces. Our experience indicates that deposit formation due to settled solids can be controlled by irrigation of the affected surfaces with water.

The crystallization of salts from supersaturated solutions can be a much more difficult problem to control. Both calcium sulphate and sulphite have strong tendencies to form supersaturated solutions from which the salts crystallize in an unpredictable way. If crystals form on the internal surfaces of the scrubber, a very hard, tenacious film is formed which tends to promote further crystallization. To control this type of scale formation, it is necessary to keep the concentrations of dissolved calcium sulphite and sulphate as low as is practical which is probably at or near the saturation level. In practice, this can be accomplished by maintaining a very high liquid to gas ratio.

Scrubbers that are designed for high gas sorption efficiency at low liquid rates, such as packed towers and flooded bed and tray types, are therefore considered unsuitable for use with the limestone slurry process, unless very high liquid rates are maintained, in which case the main advantage of these devices is lost. In the spray tower where very high liquid rates are needed to increase gas sorption efficiency, there is very little possibility of forming highly supersaturated solutions with attendant scaling problems. This has been verified in pilot plant testing where no hard scale formation has occurred during a year of operation, which included a 1000-hour continuous run. On the other hand, hard scale formation has frequently been observed in flooded bed and tray-type scrubbers.

When large liquid to gas ratios are used, coupled with low sulphur dioxide concentrations, the equilibrium back pressure of sulphur dioxide over the slurry surface is negligible. For this reason, a true countercurrent-type scrubber is not essential and a single equilibrium stage is adequate to obtain a high mass transfer rate.

A spray tower offers further advantages in handling large volumes of flue gas such as those from power plants. It has the highest turn down ratio and the lowest pressure drop of the alternatives considered. Further, it has a minimum of internal surfaces and so reduces the possibility of plugging even if scale formation does take place. Although its mass transfer characteristics are not as good as those of the other scrubbers, it is considered adequate in this respect.

DESCRIPTION OF PILOT PLANT

Figure 1 is a diagram of the pilot plant, a detailed description of which is contained in Appendix I. Four thousand cfm of flue gases at 260 F from a coal-fired boiler were drawn off after the electrostatic precipitator and passed through a spray tower and then to the stack. The spray tower was 32 inches square, 16 feet high, and contained 6 banks of sprays, each fitted with 9 full-cone spray nozzles. The slurry, containing about 12 per cent by weight of solids, was recirculated by centrifugal pumps from two interconnected 500-gallon tanks containing a total of about 900 gallons of slurry. A pH sensing probe, located near the pump feed on the recirculating tank, switched on the dry limestone feeder and the clarified liquor pump so that a mixture of fresh limestone and clarified liquor from the settling tank was added to the slurry recirculating tank each time the pH fell below the set point of 5.8. This fresh feed caused an overflow of spent slurry from the recirculating tank to the settling tank. Fresh make-up water was used to wash the demister and to flush the pump seals. There was no liquid waste stream.

The sulphur dioxide concentrations were measured by an infrared analyzer. The operating variables studied included the gas velocity, liquid to gas ratio, nozzle pressure and the slurry retention time.

RESULTS AND DISCUSSION

The results are expressed in terms of the overall mass transfer coefficient K_{ga}, the number of transfer units N_{og} and the overall efficiency of sulphur dioxide removal. In the calculations, it was assumed that the equilibrium back pressure of sulphur dioxide over the slurry surface was negligible. The following formulae were used to calculate K_{ga} and N_{og} values:

$$N_{og} = \ln y_1/y_2$$

$$K_{ga} = (G^*/V) \ln y_1/y_2$$

where: G^* is the molar flow rate of flue gas

V is the effective volume of the spray tower,

y_1 and y_2 are the inlet and outlet concentrations of sulphur dioxide.

Effect of Gas Velocity: The performance of a single bank of sprays was studied under various gas and liquid flow rates. The liquid flow rate was varied by changing the nozzle pressure. Figure 2 shows the effect of gas velocity on the mass transfer coefficient K_{ga} under various liquid flow rates when using the spray bank having nine 1/4-inch orifice nozzles. It can be seen from Figure 2 that K_{ga} increases with increasing gas velocity. The strong dependence of K_{ga} on gas velocity indicates a significant gas phase resistance to mass transfer. Figure 3 shows similar data for another spray bank containing nine 1/2-inch spray nozzles. Because of the larger orifices, more slurry could be sprayed at a given nozzle pressure than with the 1/4-inch nozzles. The marked increase in K_{ga} with gas velocity can also be seen in Figure 3. It is interesting to note that when gas velocity is increased at constant liquid flow rate, the liquid to gas ratio decreases, but in spite of this decrease, the mass transfer coefficient shows an increase. Increasing the gas velocity not only decreases the gas phase resistance, but probably decreases the liquid film resistance as well by inducing some surface regeneration of the liquid droplets.

Effect of Nozzle Pressure and Size: The effect of nozzle pressure was studied by comparing the performance of a bank with 1/4-inch orifice nozzles with that of a bank with 1/2-inch orifice nozzles. The results, given in Table I, show that under similar gas and liquid flow rates the mass transfer coefficient K_{ga} is practically unchanged in the nozzle pressure range of 10 to 20 psig. Further, the two-fold change in orifice size did not affect the mass transfer coefficient.

TABLE I

EFFECT OF NOZZLE SIZE AND PRESSURE ON MASS TRANSFER COEFFICIENT AT CONSTANT LIQUID FLOW RATES

Run No	Nozzle Orifice Size (in)	P_N (psig)	L (IGPM)	V_G (fps)	L/G (I gal/ 1000 cu ft)	K_{ga} (lb moles/hr cu ft atm)
1	1/2	10	47.5	4.79	23.65	2.09
2	1/4	20	46.5	4.79	23.15	2.06
3	1/2	10	46.0	7.19	15.23	2.26
4	1/4	20	46.5	7.19	15.40	2.30
5	1/2	10	46.0	9.47	11.98	2.75
6	1/4	20	46.5	8.97	12.34	2.83

Effect of Liquid Flow Rate: The liquid flow rate at a given gas velocity was varied by operating various spray banks simultaneously. Figure 4 shows the effect of liquid flow rate on mass transfer coefficient K_{ga} at a constant gas velocity of 8.6 ft/sec. It can be seen from Figure 4 that the liquid flow rate has a marked effect on K_{ga}. The increase in K_{ga} is due to increased gas-liquid interfacial area and the greater volume of slurry present to dissolve and react with the gas. Figure 5 shows the number of transfer units as a function liquid flow rate. Extrapolation of the linear part of the plot gives the order of magnitude of the wetted wall effect. Figure 6 shows the overall efficiency of sulphur dioxide removal as a function of liquid to gas ratio at a gas velocity of 8.6 ft/sec.

Slurry Retention Time: Retention time is defined as the time the slurry is retained in the recirculation tank before being returned to the scrubber. Some retention time is necessary to eliminate any supersaturation which may be present in the liquid at the scrubber outlet. The recirculation of supersaturated solutions increases the probability of scaling. The length of retention time also affects the pH recovery of the slurry. A plot of typical pH recovery of a sample of slurry taken at the scrubber outlet is shown in Figure 7. The exact shape of this curve is dependent upon the nature of the limestone, its particle size, the solids concentration in the slurry and the amount of sulphur dioxide absorbed per unit volume of slurry. Some experiments were also conducted to study the effect of pH recovery on the mass transfer rate. The results are shown in Table II. A decrease in mass transfer coefficient with decreasing retention time was noted, probably due to the lowering of the pH of recirculating slurry.

TABLE II

EFFECT OF RETENTION TIME ON MASS TRANSFER RATE

Run No	R_t (mins)	L (IGPM)	V_G (fps)	K_{ga} (lb moles/hr cu ft atm)
1	17.2	49.0	7.19	1.42
2	8.6	49.0	7.19	1.20
3	8.5	99.0	7.19	1.98
4	4.3	99.0	7.19	1.75
5	5.7	146.5	7.19	2.98
6	2.9	146.5	7.19	2.59
7	4.2	196.5	7.19	3.72
8	2.2	196.5	7.19	3.18

General Operating Experience

Operation of the pilot plant was automatic except for filling the limestone feeder hopper and discharging the spent sludge from the settling tank. The process was controlled by monitoring the pH of the slurry. The limestone feed was automatically turned on when the pH in the slurry recirculation tank dropped below 5.8 and was turned off when the pH was 5.8 or more. The limestone consumption was from 1.2 to 1.3 times the stoichiometric amount. A typical composition for the slurry is given in Table III.

During the pilot plant operation, which included a 1000-hour continuous run, deposits accumulated in the demister and in the flue gas inlet zone. These deposits were soft and were easily removed by water jets or mechanical scraping. The chemical compositions of the deposits are given in Table III. The deposit in the demister zone contained mainly calcium sulphate along with calcium carbonate and fly ash. The deposit in the gas entry zone contained about equal amounts of fly ash and calcium salts. The scrubber shell was found to be remarkably free of scale and deposits. The spray banks were also free of deposits except for the top two banks which were used infrequently. Deposits usually occurred on surfaces which were not adequately irrigated with slurry or water.

The bulk settling rate of the spent slurry was approximately three inches per hour and gravity settling gave a sludge containing about 35-40 per cent solids by weight. This could be dewatered to approximately 80 per cent solids by vacuum filtration. The sludge could be discharged directly into a settling pond but, if the sludge has to be transported for disposal, some conditioning might be necessary to improve its handling properties. Even after vacuum filtration, the sludge is semi-plastic and when jarred or vibrated forms a uniform levelled mass.

The average pressure drop through the spray tower including the demister was about 0.5 to 1.0 inch of water.

TABLE III

CHEMICAL COMPOSITION OF SOLIDS IN THE SLURRY AND THE DEPOSIT SAMPLES

	Calcium Sulphate	Calcium Sulphite	Calcium Carbonate	Balance ash,etc
	Per Cent by Weight			
Typical Recirculating Slurry	30	56	12	2
Demister Deposit	74	--	3	23
Gas Inlet Deposit	30	4	15	51

CONCLUSIONS

- A spray tower is suitable for scrubbing large volumes of flue gases with limestone slurry. From 70 to 80 per cent of the sulphur dioxide can be removed from the flue gases and, although considerable energy is needed for pumping the slurry, the gas phase pressure drop across the tower is very low.
- The mass transfer coefficient is a direct function of both gas velocity and the liquid flow rate. The increase in mass

transfer coefficient with increasing gas velocity is of particular interest and may lead to reducing the size of the spray tower.

- Deposit formation in the scrubber can be prevented by irrigating surfaces with slurry or make-up water and by limiting the degree of supersaturation in the liquid phase.
- The consumption of limestone can be kept within 1.2 to 1.3 times the stoichiometric requirement by maintaining the pH of the recirculating slurry between 5.6 and 5.8.

LIST OF SYMBOLS

a - gas-liquid interface, sq ft/cu ft of active scrubber volume

G - gas flow rate, cu ft/hr at 120 F

G^* - molar gas flow rate, lb moles/hr

K_{ga} - mass transfer coefficient, lb moles of SO_2/hr cu ft of scrubber volume/atm of driving force

L/G - liquid to gas ratio, I gal/1000 cu ft of flue gas at 120 F

N_{og} - number of transfer units

P_N - nozzle pressure of the slurry, psig

R_t - retention time, defined as the time the slurry is retained in the recirculation tank before being returned to the scrubber, minutes

V_G - gas velocity through the scrubber shell, ft/sec

y_1, y_2 - concentration of sulphur dioxide in the gas at the scrubber inlet and outlet, ppm by volume

APPENDIX I

PILOT PLANT DESCRIPTION

Figure 1 is a diagram of the pilot plant. Flue gas was drawn from the main duct, after the electrostatic precipitator, and through the scrubber shell by an induced draft fan (F1). The flue gas entered the scrubber at about 260 F. After scrubbing it was cooled to about 120 F and discharged to the atmosphere from a 25-foot-high chimney. The gas flow rate was regulated with a damper (D1) and was monitored with a pitot tube. The 32-inch-square scrubber was constructed from 1/16-inch-thick 316 stainless steel sheet. The shell was assembled in 7 flanged sections with a total height of 16 feet. The bottom section was conical and a chevron-type demister was installed in the top section. The slurry was sprayed into the tower from 6 spray banks (S1-6). The top 4 banks sprayed counter-currently to the gas flow and the bottom 2 sprayed cocurrently. Each bank was equipped with 9 full-cone spray nozzles arranged to completely cover the tower cross section with spray. The top bank had 1/2-inch orifice nozzles and the remaining banks had 1/4-inch orifice nozzles. These nozzles when operated under 10-20 psig pressure gave a spray angle of about 80 degrees with an average drop size of 2500 microns. The slurry flowed out of the tower through the bottom conical section and a 6-inch discharge pipe which was immersed in the slurry tank (T1) to provide a liquid seal.

The slurry, containing about 12 per cent solids, was recirculated from 2 interconnected 500-gallon tanks (T1 & T2) containing about 900 gallons of slurry. This capacity was chosen to provide a minimum of 3 minutes delay time in the tank for the recirculating slurry. The slurry in the tanks, kept in suspension by paddle-type agitators (A1 & A2), was recirculated by three centrifugal pumps (P1-3). The slurry flow through the banks was regulated with diaphragm valves and metered through orifice plates.

Limestone was added to the recirculating slurry automatically using a pH control system. A pH sensing probe, placed near the pump suction in tank (T2), operated a screw-type limestone feeder (F1) and the clarified liquor recirculating pump (P4). The dry limestone feed was mixed with the clarified liquor in a mixing cone (C1) and introduced near the bottom of tank (T1). Spent slurry was discharged from an overflow in tank (T1) into the settling tank (T3). The settled sludge containing 35-40 per cent solids was pumped into the station's settling pond.

The sulphur dioxide in the flue gas before and after the scrubber was monitored with an infrared analyzer. The moisture content of the incoming gas was determined by wet and dry bulb temperature readings. The make-up water was used for demister washing and flushing pump seals.

APPENDIX II

TABLE IV

SUMMARY OF DATA OBTAINED WITH BANK NO 4 (NINE 1/4-INCH ORIFICE FULL-CONE SPRAY NOZZLES, COUNTERCURRENT

un o	P_N (psig)	L (IGPM)	V_G (fps)	L/G (I gal/ 1000 cu ft)	SO_2 Conc (ppm)		% SO_2 Removed	K_{ga} (lb moles/hr cu ft atm)
					In Gas	Exit Gas		
1	25	52.0	4.8	25.9	1080	500	53.7	2.20
2	25	52.0	7.2	17.2	1170	650	44.4	2.54
3	25	52.0	9.0	13.8	1170	675	42.3	2.98
4	20	46.5	4.8	23.2	1075	525	51.2	2.06
5	20	46.5	7.2	15.4	1150	675	41.3	2.30
6	20	46.5	9.0	12.3	1180	700	40.6	2.84
7	15	41.5	4.8	20.7	1100	575	47.7	1.86
8	15	41.5	7.2	13.8	1180	725	38.7	2.11
9	15	41.5	9.0	11.0	1180	750	36.5	2.45
0	10	33.5	4.8	16.7	1200	710	40.8	1.51
1	10	33.5	7.2	11.1	1300	875	32.7	1.72
2	10	33.5	9.0	8.9	1320	925	29.95	1.92

APPENDIX II (Cont'd)

TABLE V

SUMMARY OF DATA OBTAINED WITH BANK NO 6
(NINE 1/2-INCH ORIFICE FULL-CONE SPRAY NOZZLES, COUNTERCURRENT

Run No	P_N (psig)	L (IGPM)	V_G (fps)	L/G (I gal/ 1000 cu ft)	SO_2 Conc (ppm)		% SO_2 Removed	K_{ga} (lb moles/hr cu ft atm)
					In Gas	Exit Gas		
1	25	86.0	4.8	42.8	1500	550	63.4	2.87
2	25	86.0	7.2	28.5	1600	780	51.2	3.10
3	25	89.5	9.5	22.4	1525	725	52.5	4.09
4	20	78.0	4.8	38.9	1500	560	62.6	2.83
5	20	74.5	7.2	24.9	1560	780	50.0	2.99
6	20	78.0	9.5	20.3	1620	810	50.0	3.80
7	15	60.0	4.8	29.9	1500	650	56.6	2.40
8	15	61.5	7.2	20.4	1560	840	46.1	2.66
9	15	64.0	9.5	16.7	1620	900	44.5	3.23
10	10	47.5	4.8	23.7	1450	700	51.7	2.09
11	10	46.0	7.2	15.2	1560	925	40.7	2.26
12	10	46.0	9.5	12.0	1600	970	39.3	2.75

TABLE VI

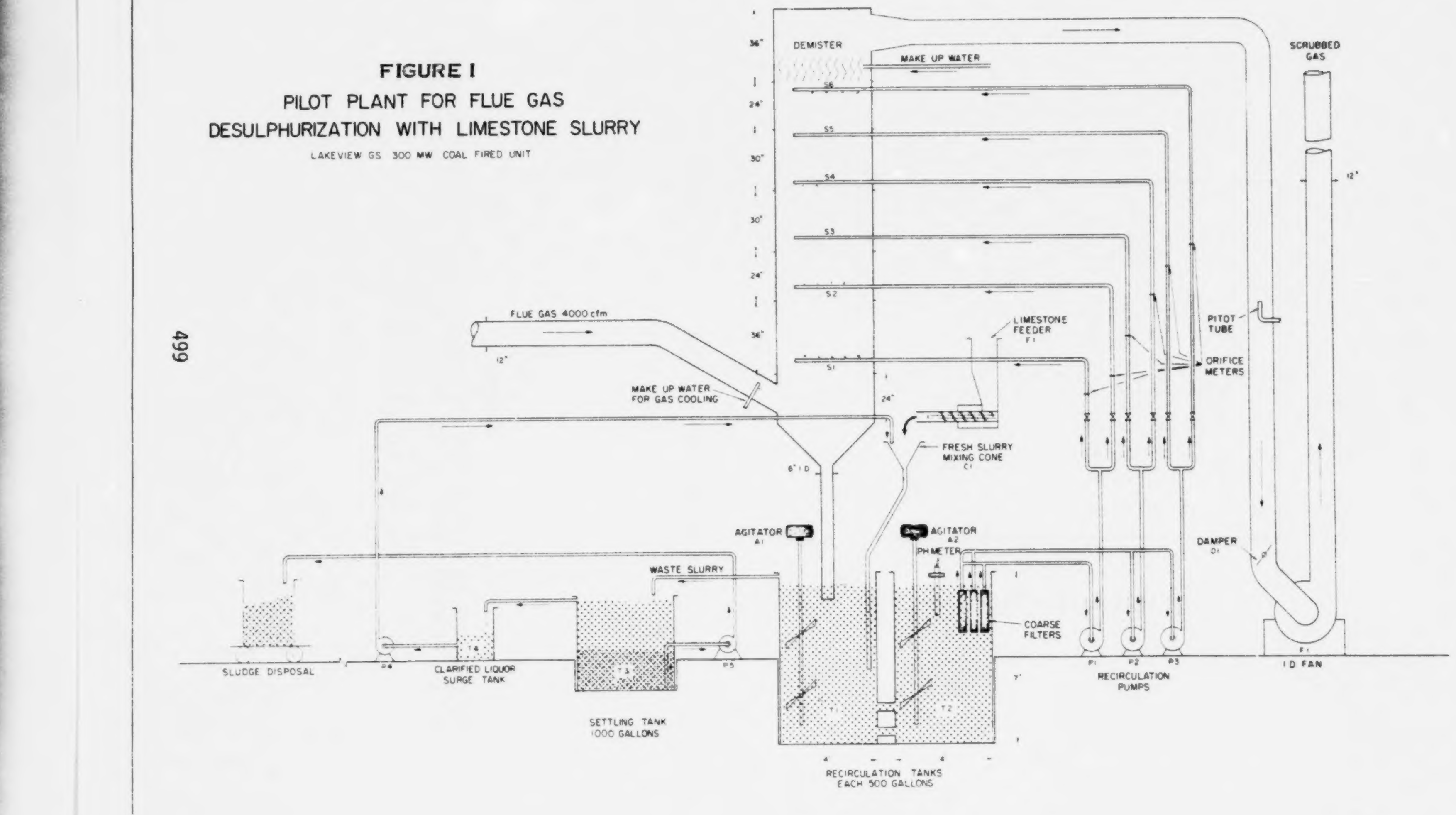
SUMMARY OF DATA OBTAINED OPERATING VARIOUS BANKS SIMULTANEOUSLY

Run No	L (IGPM)	V_G (fps)	L/G (I gal/ 1000 cu ft)	SO_2 Conc (ppm)		% SO_2 Removed	N_{og}	K_{ga} (lb moles/hr cu ft atm)
				In Gas	Exit Gas			
1	50	8.6	13.9	1020	600	41.2	0.53	2.75
2	100	8.6	27.7	1020	410	59.8	0.91	4.71
3	136	8.6	37.4	1020	340	66.7	1.10	5.68
4	186	8.6	51.5	1030	290	71.9	1.27	6.54
5	232	8.6	64.2	1030	210	79.6	1.59	8.71
6	282	8.6	78.1	1040	170	83.7	1.81	9.36

FIGURE I

PILOT PLANT FOR FLUE GAS
DESULPHURIZATION WITH LIMESTONE SLURRY

LAKEVIEW GS 300 MW COAL FIRED UNIT



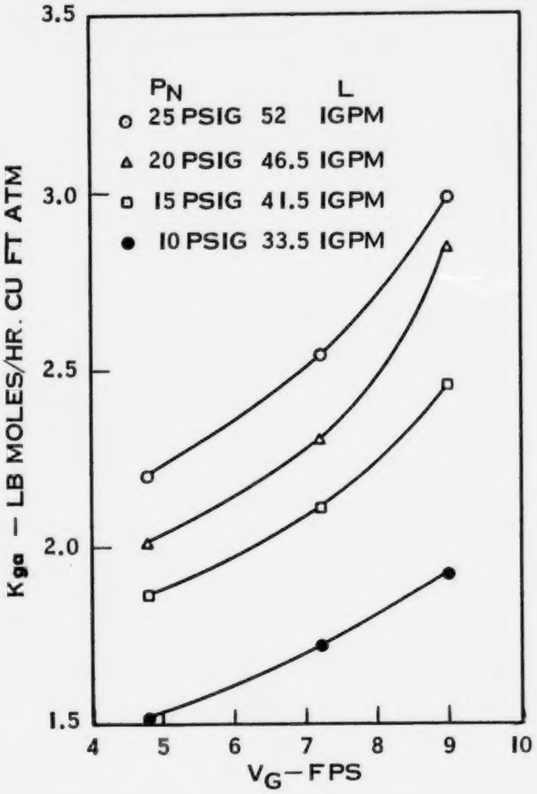


FIGURE 2

EFFECT OF GAS VELOCITY ON MASS TRANSFER COEFFICIENT AT DIFFERENT LIQUID FLOW RATES AND NOZZLE PRESSURES
(BANK S–4, COUNTERCURRENT)
(ORIFICE DIA OF NOZZLE = 1/4")

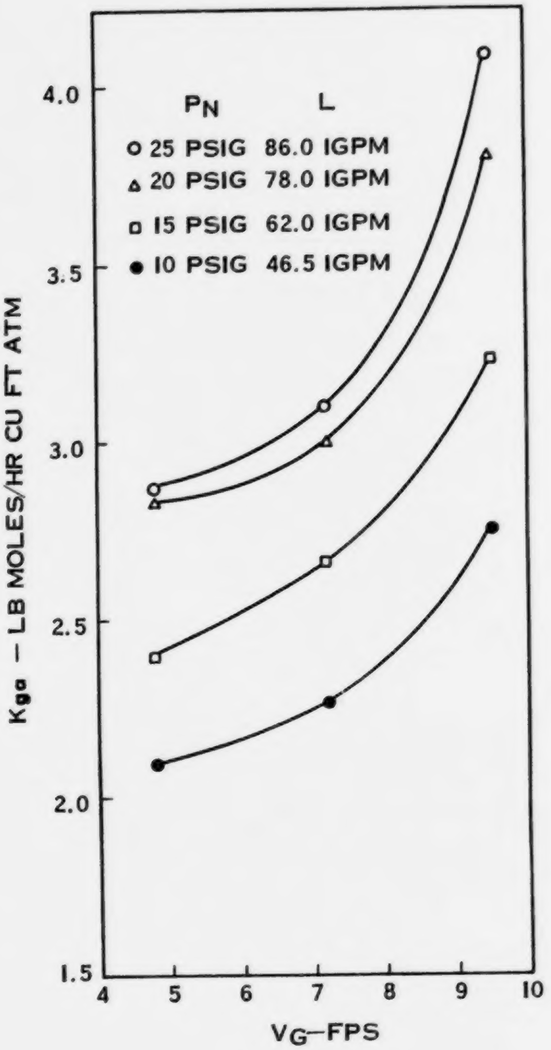


FIGURE 3

'EFFECT OF GAS VELOCITY ON MASS TRANSFER COEFFICIENT
AT DIFFERENT LIQUID FLOW RATES AND NOZZLE PRESSURES
(BANK S–6, COUNTERCURRENT)
(ORIFICE DIA OF NOZZLE = 15/32")

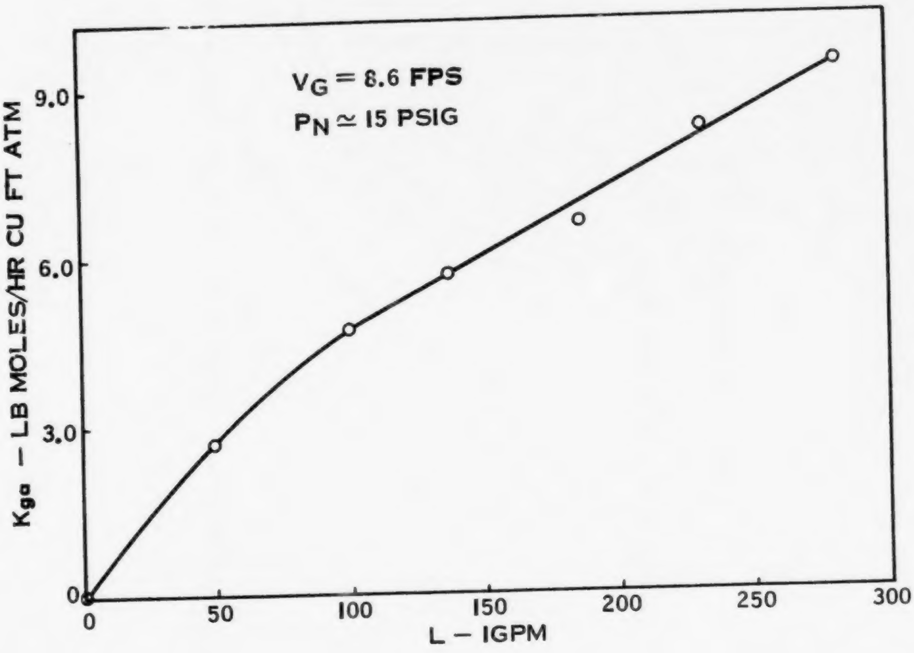


FIGURE 4

EFFECT OF LIQUID FLOW RATE ON MASS TRANSFER COEFFICIENT AT CONSTANT GAS VELOCITY AND NOZZLE PRESSURE

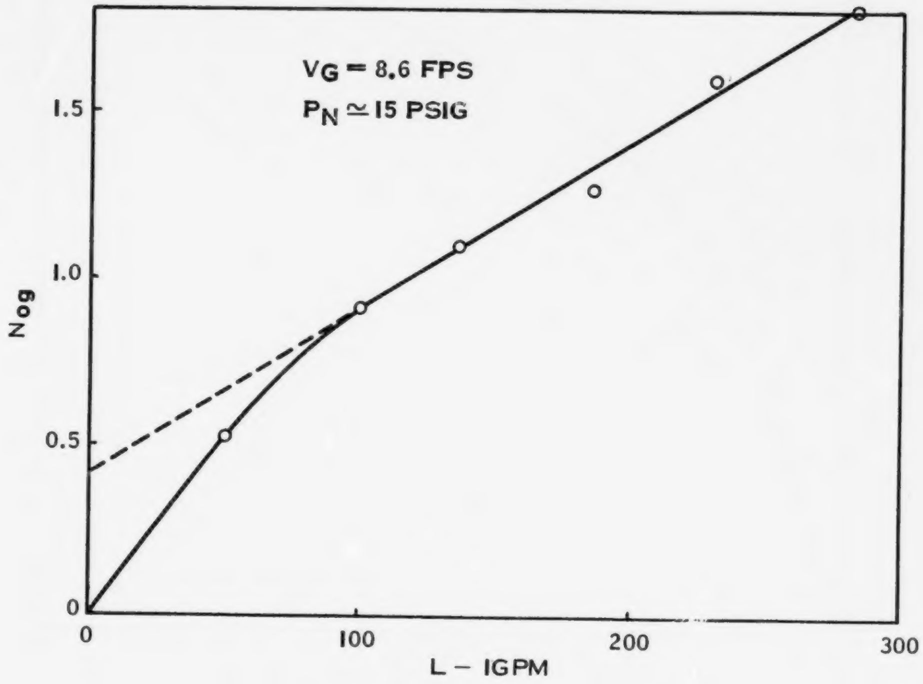


FIGURE 5

EFFECT OF LIQUID FLOW RATE ON THE NUMBER OF TRANSFER UNITS AT CONSTANT GAS VELOCITY AND NOZZLE PRESSURE

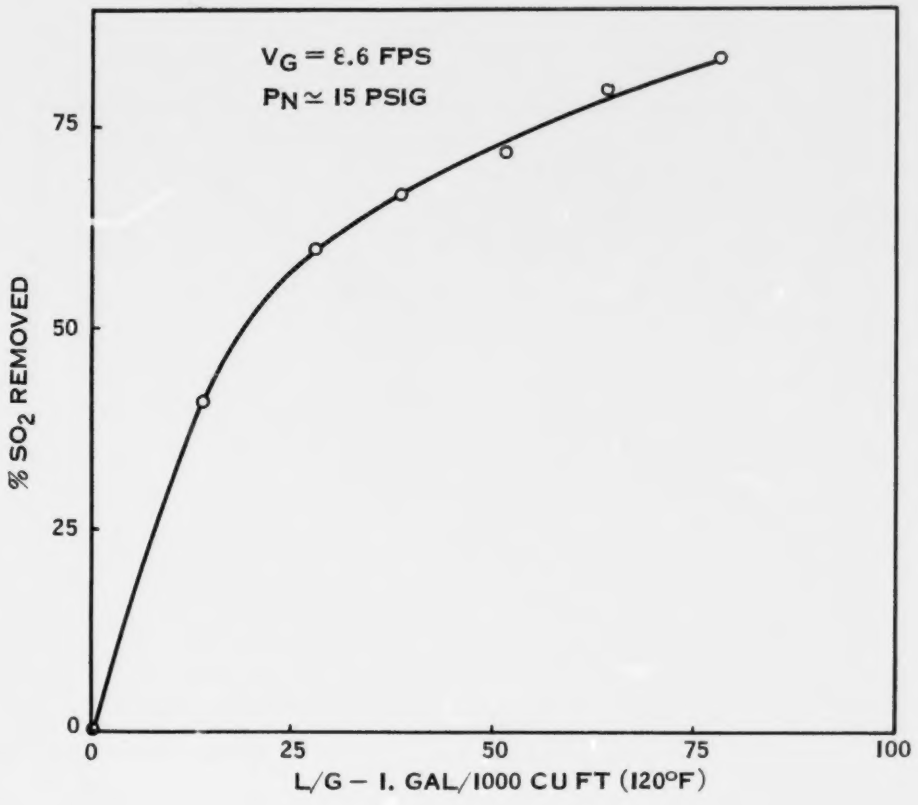


FIGURE 6

EFFECT OF L/G ON THE EFFICIENCY OF SULPHUR DIOXIDE REMOVAL AT CONSTANT GAS VELOCITY AND NOZZLE PRESSURE

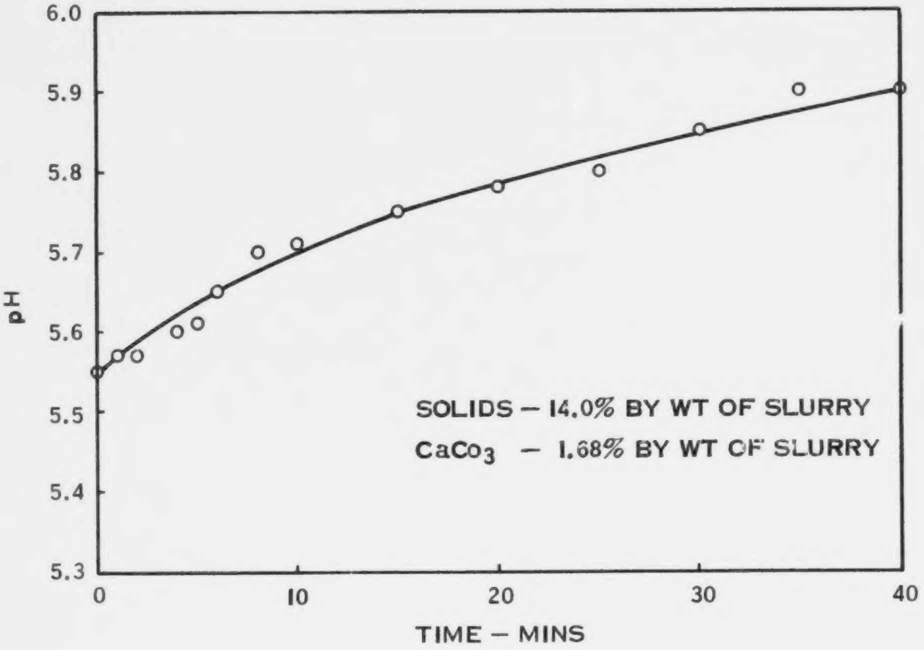


FIGURE 7

pH RECOVERY OF SPENT SLURRY

THE MOHAVE/NAVAJO PILOT FACILITY
FOR
SULFUR DIOXIDE REMOVAL

BY

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I. INTRODUCTION

The Mohave/Navajo SO_2 Removal Research Program is a project for testing alkali absorption processes on a pilot-size basis. The major thrust of the work is to determine the characteristics of these processes as applied to boilers fired with low-sulfur coal.

The program was initiated in June 1970. The owners of the Navajo Generating Station, which is under construction near Page, Arizona, asked the Bechtel Corporation (engineers-constructors of the Station) to survey the status of SO_2 removal technology for application to the Station. Schedules call for initial operation of each of three 770 Mw units in 1974, 1975, 1976, respectively.

Coal dedicated to Navajo will come from the Black Mesa mine. Surveys have indicated that over the life of the plant, this coal will have sulfur content varying from about 0.3% S to 0.8% S with an average of about 0.5%. The heating value of this sub-bituminous coal is about 11,000 BTU/lb.

We need not, for this audience, describe the state of technology that we observed in the Summer of 1970. However, it is worthy of note that there was considerable surprise evidenced in the industry that utilities with such very low sulfur coal were seriously considering sulfur dioxide removal. The concerns of the industry had been directed towards reducing flue-gas concentrations of sulfur dioxide to levels approaching the

400 ppm that are the expected values for Navajo at the boiler outlet. Therefore, relatively little was known concerning the performance that could be achieved, the operational problems that might be expected when attempting to reduce concentrations of SO_2 from 400 ppm on down, or the economic trade-offs involved.

Incidentally, events during the past year have shown that while Western utilities have access to low-sulfur coals, they may still be required by state emission regulations to apply flue-gas absorption equipment.

Another feature distinguishes the approach adopted for the Navajo Station from many others. High efficiency particulate removal equipment will be located upstream of the SO_2 absorption equipment, so that the designs and constraints of the system will be based almost completely on SO_2 absorption.

These facts shaped the basic nature of the research program that we describe here.

The characteristics of the Navajo Station are very similar to those of the Mohave Generating Station. The latter consists of two 770 Mw units which also burn Black Mesa coal. Both units of the Mohave Station have been completed. Therefore, the owners of the two stations have joined in sponsoring this experimental program located at Mohave. Southern California Edison Company was selected by the participating owners as Project Manager of the program.

A flexible, dual-loop system was designed and installed at Mohave. Construction was completed in July, 1971. As it was desired to test as many different types of absorbers as possible in a short time, two identical testing loops were built, each with individual controls and instrumentation. In each loop provision was made for installation of two absorbers in parallel with ducting that could pass the flue gas through either one. At the present time, the four absorbers installed contain a single stage venturi, a turbulent contact absorber, a combined Lurgi-impingement tray, and a low pressure-drop egg-crate packing, respectively.

The Mohave units have electrostatic precipitators that are operating at very high efficiency. Ducting inlets to the test loops were placed both upstream and downstream of the precipitators so that the effects of particulate loading can be tested. As we shall show, the process loops are designed to simulate on a small scale, the operations that a full-scale unit may be required to undergo.

Downstream of each absorber is an electrically powered flue-gas reheater, installed mainly to enable measurement of the demister efficiencies.

The present program plan provides for testing three absorbents - limestone slurry, lime slurry, and soda-ash solution. Parametric variations of L/G, gas flow rate, and pH are made, while measuring SO_2 absorption efficiency and particulate removal. In addition the possibility of regenerating the soda-ash absorbent (using lime) is being investigated.

II. PILOT PLANT DESCRIPTION

The pilot plant facility is constructed on three skid-mounted platforms as shown in Figures 1 and 2. It accommodates the four previously mentioned scrubbers and the two identical loops which take a flue gas sidestream of 500 acfm to 4000 acfm from the Mohave Station (Unit 1) exit duct. A 10' x 50' trailer equipped with control panels is at one quadrant of the pilot plant. The trailer also contains a wet chemistry laboratory with chemical analysis equipments and an atomic absorption spectrometer, permitting analyses on-site.

Figure 3 shows the flow diagram. The sample flue gas is withdrawn, by the suction generated by a 20" fan, from either upstream or downstream of the electrostatic precipitator. Special care was taken in designing the sampling valve for the gas intake at the electrostatic precipitator upstream line in an attempt to obtain representative fly ash concentration at all flow rates. At the downstream of the precipitator, since the fly ash distribution consists mainly of small particles, the gas is withdrawn through a simple 14" collecting elbow parallel to the main gas flow. The gas flow rate up to 4000 acfm automatically is controlled by an orifice flow controller through a butterfly valve in the gas line to the blower.

Upon entering the gas system of the pilot plant, the flue gas is automatically monitored for gas temperature, pressure at many key points, and SO_2, NO_x and O_2 concentrations at locations in and out of the scrubber. Dust loadings of the feed stream and the effluent stream of the scrubber are periodically measured by manually collecting gas samples.

The flue gas from the scrubber passes through an electric preheater which is controlled by a temperature controller. Heat input of the reheater is accurately monitored so that by heat balance, the quantity of entrained liquid can be calculated. The gas is then discharged through a short stack.

For the measurement of SO_2, NO_x and O_2 concentrations, the on-line monitoring system has its own gas circuit shown in Figure 4. The gas is sampled through a microporous dust filter in the collecting point and a condensate trap prior to entering into the electrochemical cells. Shutoff valves and air-back-purge are provided for cleaning the filter if necessary. Electric time and solenoid valves are used to switch alternately from one gas to the other so that one set of analyzers can be used to monitor both feed and effluent streams. Standardized gas mixture is used to calibrate the electrochemical cell periodically.

For the measurement of dust loading in the gas in and out of scrubber, fiber glass filters for total mass and inpaction-type particle classifiers for size distribution are employed.

The four types of absorbers to be tested are as follows:

A. Turbulent Contact (UOP)

A 19-inch ID by 27-foot height absorber, with three trays of mobile packing (each tray containing 850 of pinch ping-pong balls) and a 24-inch-square demister section. It is rated at 1500 cfm and requires up to a 60-gpm solution circulation rate (stainless steel construction).

B. Venturi (Chemico)

A 30-inch ID Venturi (6-1/16 inch to 7-1/8 inch throat) scrubber, with a 30-inch ID centrifugal separating chamber. It is rated at 1500 cfm and requires 30- to 60-gpm solution circulation (stainless steel construction).

C. Polygrid Packed (Heil)

A 24-inch ID by 15-foot-high Heil absorber, which will be tested with a 7-foot depth of polygrid (Ecodyne Corporation, formerly Fluor Products Company) "eggcrate" packing. It is rated at 2000 to 3000 cfm and required 25- to 50-gpm solution circulation (fiberglass scrubber, polypropylene packing).

D. Lurgi Impingement (Peabody)

A 30-inch ID by 14-foot-high scrubber, combining a Lurgi Venturi and three Peabody impingement trays. It is rated at 1500 to 2000 cfm and requires 40- to 50-gpm solution circulation (stainless steel construction).

The liquor flow rate to each scrubber is controlled by a magnetic flow recorder-controller in the 3" main PVC line from the hold tank. A liquid level controller is provided in the hold tank to adjust the tank volume to allow sufficient hold time for the supersaturated calcium sulfite slurry from the scrubber to desupersaturate. A hold tank of 3-15 minutes can be achieved with the equipment sizes selected. To control solids content and to maintain a constant alkalinity and pH control in the liquor to the scrubber, a continuous withdrawal of liquor is necessary for solids removal or for regeneration. For this purpose, a centrifuge is provided for loop A while a settling tank with a long winding channel is in use for loop B.

The discharge stream from each loop is measured and analyzed before respectively flowing to the centrifuge or settling tank with the treated solution being returned continuously to maintain close solids and pH controls. The solids in loop A are processed continuously during the test, while the solids in loop B are accumulated in the bottom of the settling tank and measured before being sent to the centrifuge at the end of the test.

For the testing of both calcium and sodium absorbents in the removal of SO_2 from flue gases somewhat different process systems are required due to different solubility of these absorbents in water. In the calcium system, the scrubbing liquor contains fine particles of absorbents and is circulated through the scrubbers as a slurry. On the other hand, the sodium absorbent is passed through the system in the dissolved state, with only a small percentage of fly ash as solids.

In the System I mode of operation, as shown in Figure 5, the SO_2 is absorbed from the flue gas by either a lime or limestone slurry that is circulated to the scrubbers from the hold tank, fed from one of the two lime-limestone feed tanks. The rate of product withdrawal is controlled by a specific gravity controller in the hold tank which activates a valve to the centrifuge. The liquid level in the hold tank is adjusted by a level controller connected to the makeup water line. This level, in combination with the liquid circulation rate, is used to maintain hold time up to 10 minutes or more.

In the System II mode of operation, as shown in Figure 6, the SO_2 is absorbed from the flue gas by a sodium solution circulated to the scrubbers from the hold tank. The rate of product withdrawal from the hold tank is controlled by a pH recorder controller located in the liquid line from the hold tank. The regeneration in the reaction tank is controlled by a pH recorder-controller. Liquid in the reaction tank is pumped with level control into the centrifuge. The liquid from the centrifuge (which constitutes the regenerated sodium sulfite absorption solution) flows by pressure back into the hold tank.

III. ANALYSIS PROCEDURES

Test procedures of some of the more complicated data measurements are as follows:

A. Analyses of Gas Streams

1. SO_2 Concentration

SO_2 in the inlet and outlet gases is measured continuously by a Dynascience monitoring instrument that utilizes an electrochemical transducing cell. This unit is routinely calibrated with a standard gas mixture. Periodically, the accuracy of SO_2 analyzer is checked either by the iodometric method or by the barium sulfate turbidimetric method.

2. NO_x Concentration

NO_x in the inlet and outlet gases is measured continuously by another Dynascience monitoring instrument. This unit is calibrated routinely with a gas mixture, and its accuracy is checked by a modified phenol disulfonic acid method.

3. Dust Loading

Particulates in the inlet and outlet gases are measured in duplicate for each test Isokinetic sampling is used. Particulate mass is composed of the solids (dried to constant weight at 110C) caught on the filter thimbles or filter pads, including particulates deposited in the filter probe and sample lines. The filter pads used in the outlet gas have a reported efficiency of 99.7 percent for 0.3 particulates.

4. Trace Metals

Small amounts of metallic elements, such as mercury and chromium may be present in the inlet and outlet gases and are measured by a Varian Techtron Atomic Absorption Spectrophotometer. These elements are measured in both the particulate filtered from the gases and in the impinger liquids through which the gases pass after flowing through the filters.

5. SO_3 Concentration

A gravimetric method of determining SO_3 in the flue gas is used. The method involves collecting gas samples in two fractions: the condensate and the isopropy alcohol scrubber. The absorbed SO_3 is precipitated as barium sulfate using barium chloride.

6. Fluorine Concentration

Part of the fluorine contained in the coal, present in the flue gas, is condensed or absorbed in the traps of the SO_3 apparatus. The contents in these traps is combined and analyzed by a SPADNS--zirconium spectrophotometric method.

B. Analyses of Liquor Streams

The pH is measured continuously by an industrial pH meter, which is routinely calibrated with standard buffer solution; density is recorded continuously by a differential pressure transmitter located in the hold tank. This unit is checked periodically by gravimetric methods. Na, Ca, Cr, and other cations in the solutions are measured by the atomic absorption unit. SO_2 concentration (sulfite + bisulfite) is measured by iodometric titration. Spectrophotometric methods are used for SO_4, NO_3, etc. Sulfate determination is also confirmed by barium gravimetric method.

IV. TEST PLAN

The test plan is divided into four parts

A. Startup of pilot plant includes check-out of facility and equipment and calibration of instrumentation systems, both manual and automatic controls.

B. Initial reference experiments using blowdown water from cooling towers (8 experiments)

C. Parametric Experiments (228 experiments)

D. System Performance Tests (2 tests)

The test plans are scheduled for testing for two levels of pH (7, 9), three levels of liquid to gas ratio (3.3 to 100) and gas flow rate (500 acfm - 3000 acfm). The range over which the gas, liquid, and L/G vary differs with each type of scrubber. For each scrubber, maximum allowable ranges of gas, liquid, and L/G are tested.

The system performance tests involve two extended runs, each lasting two weeks in duration, for testing system performance from the viewpoints of erosion, corrosion, and scaling.

The parametric experiments and system performance data are to provide essential comparative data for each of the absorbers and absorbents tested.

In order to acquire meaningful experimental data for subsequent analysis, operating variables and their responses throughout the scrubbing system are measured, during each run. The relevant experimental data collected include: (1) gas flow rate; temperature; absolute pressure; pressure differential across the scrubber; SO_2, SO_3, and NO_x concentrations; and dust loadings of the feed and effluent gases; (2) absorbent liquid circulation rate; pH; temperature; and chemical composition; (3) liquid composition of feed and effluent of the regeneration tank; (4) slurry density in solids and desupersaturation time in the hold tank; (5) water losses and water droplet entrainment; and (6) quantity and composition of makeup water and absorbent feed.

The experimental data obtained from each scrubber are analyzed to assess the validity of the assumptions adopted for the mathematic model describing the behavior in each scrubber. Further, scrubber performance data such as SO_2 and particulates removal efficiencies and pressure drop across the scrubber are correlated as a function of operating parameters such as gas flow rate, L/G ratio, pH, etc., for each scrubber absorbent combination.

V. CONCLUSION

The utilities sponsoring this research feel a sense of urgency which has made the program highly specific and compressed in time. The testing, initiated in July, 1971, will be completed by March, 1972.

We believe that the results will add significantly to the body of information on alkaline wet absorption and will be of particular value to those using low-sulfur fuel.

FIGURE 1

GENERAL PLANT ARRANGEMENT
SO_2 REMOVAL PILOT PLANT

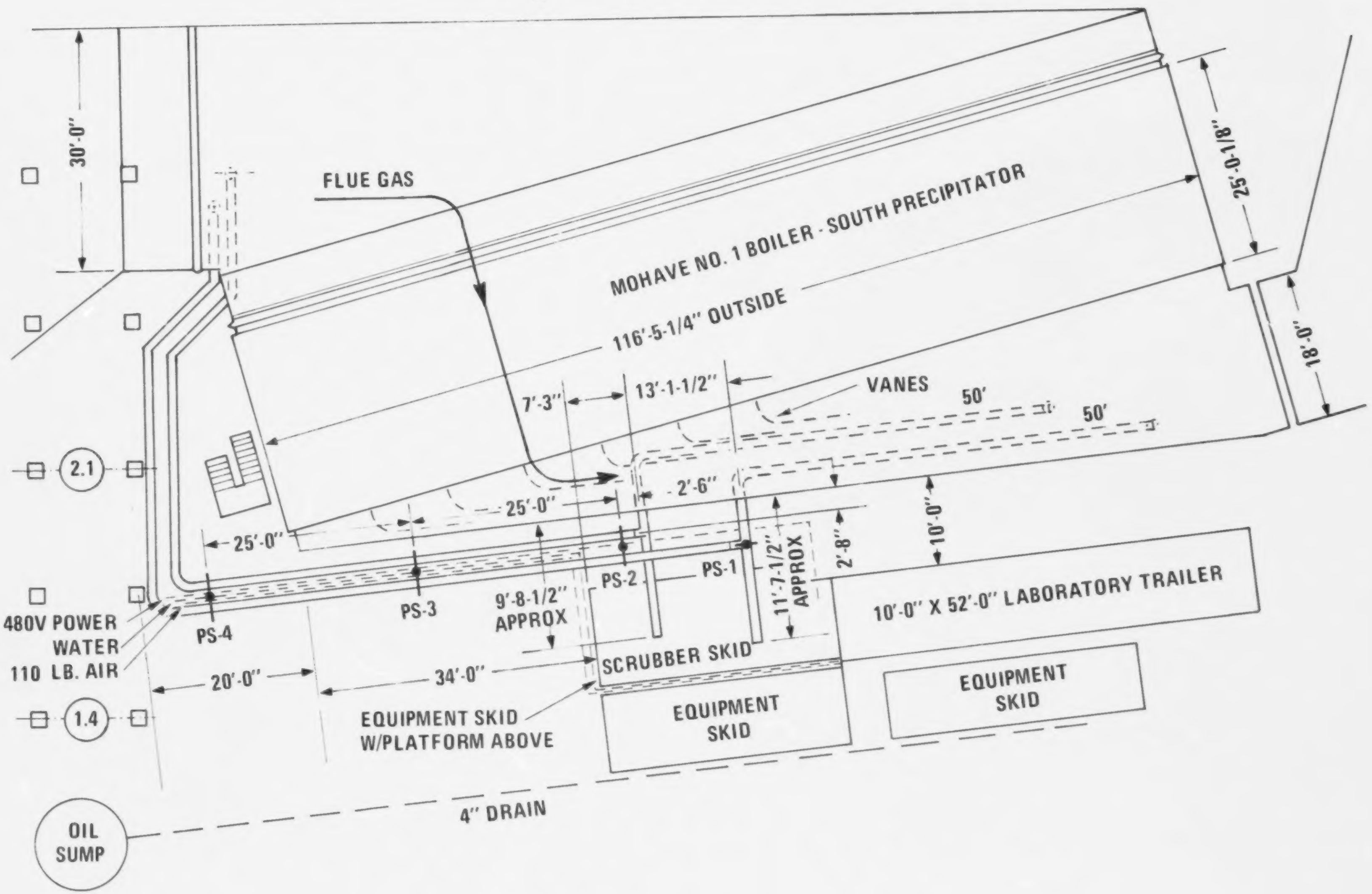


FIGURE 2

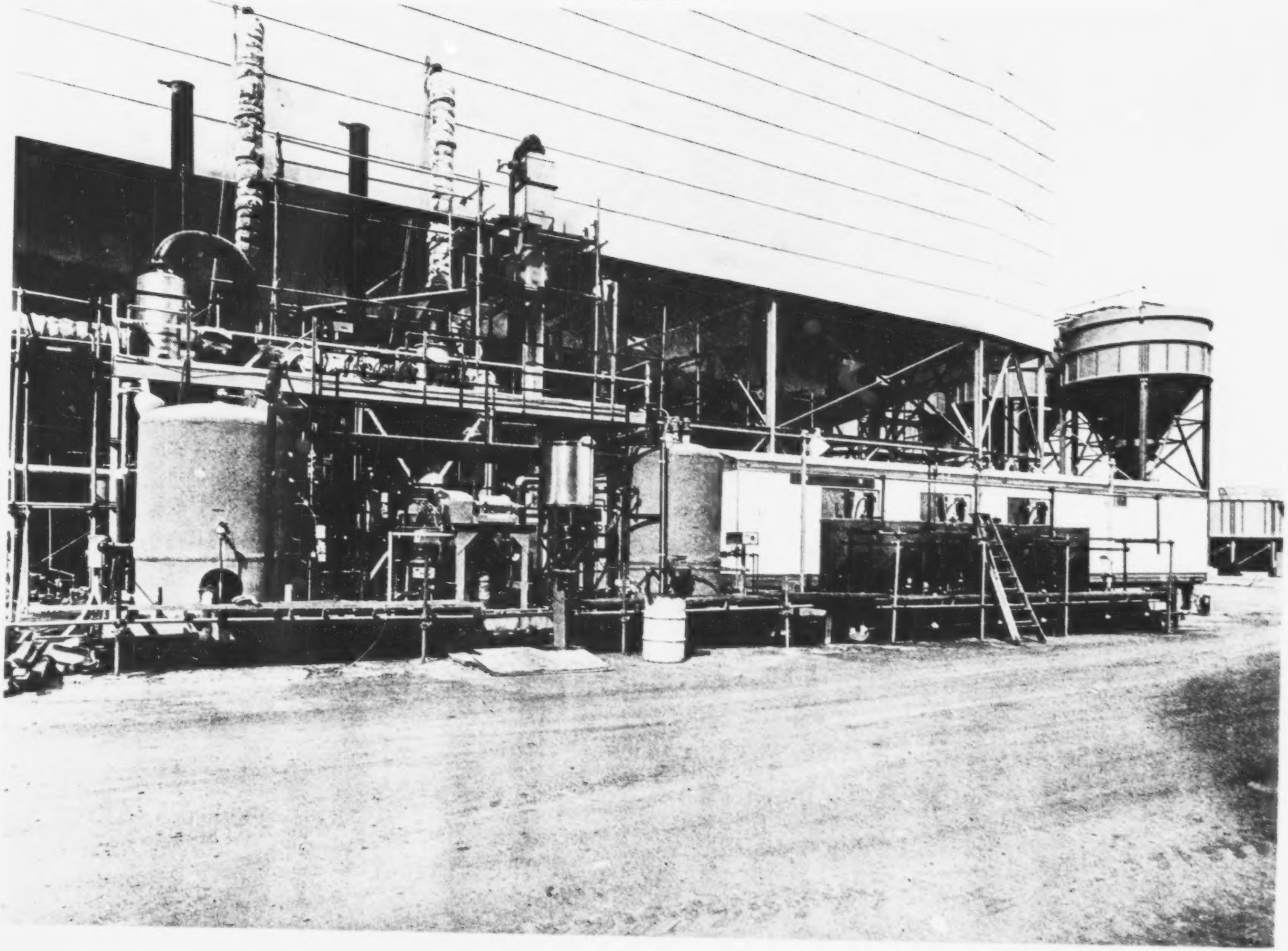


FIGURE 3

GENERAL FLOW DIAGRAM SO_2 REMOVAL PILOT PLANT

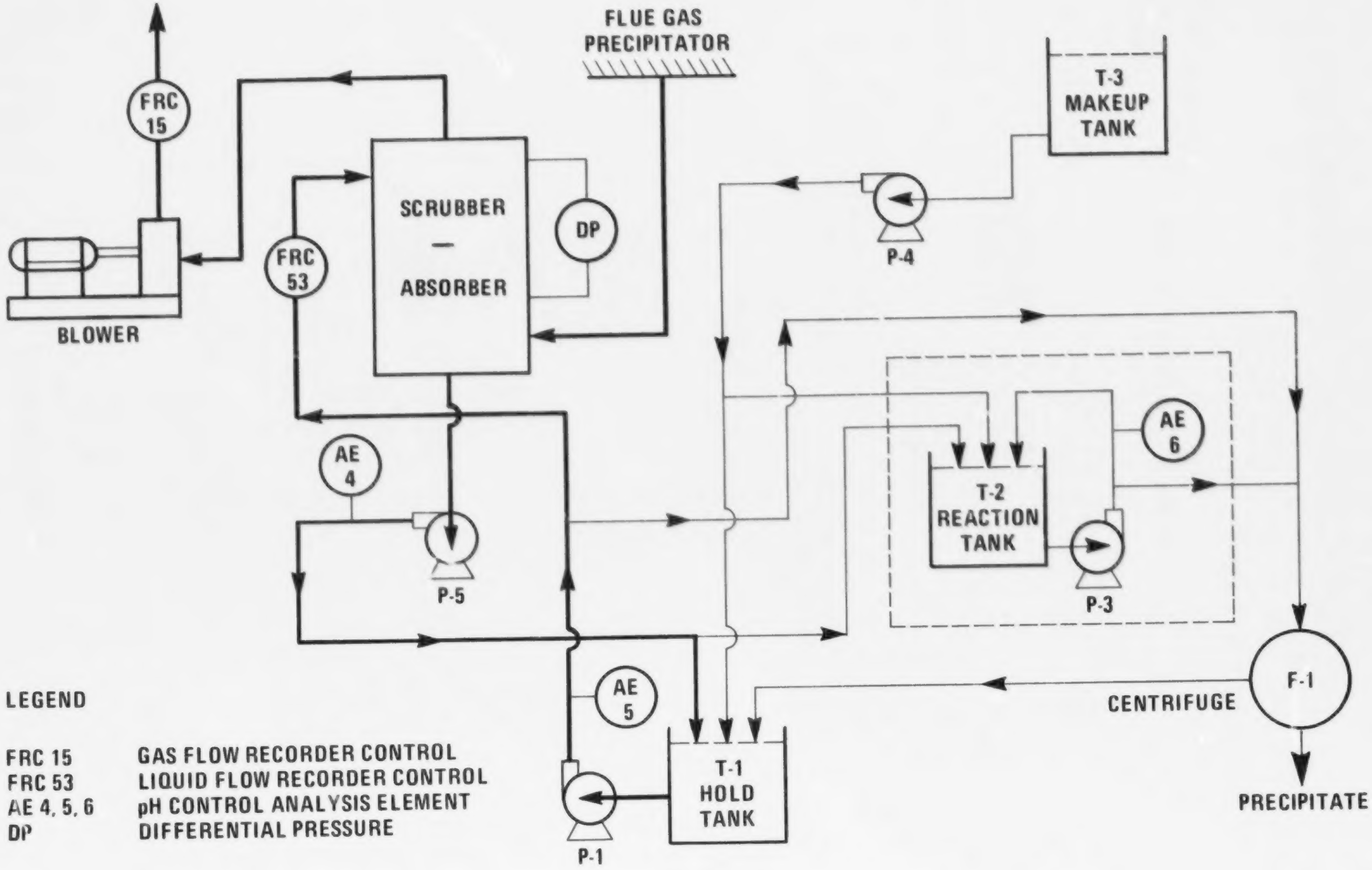


FIGURE 4

PILOT PLANT GAS MONITORING SYSTEM

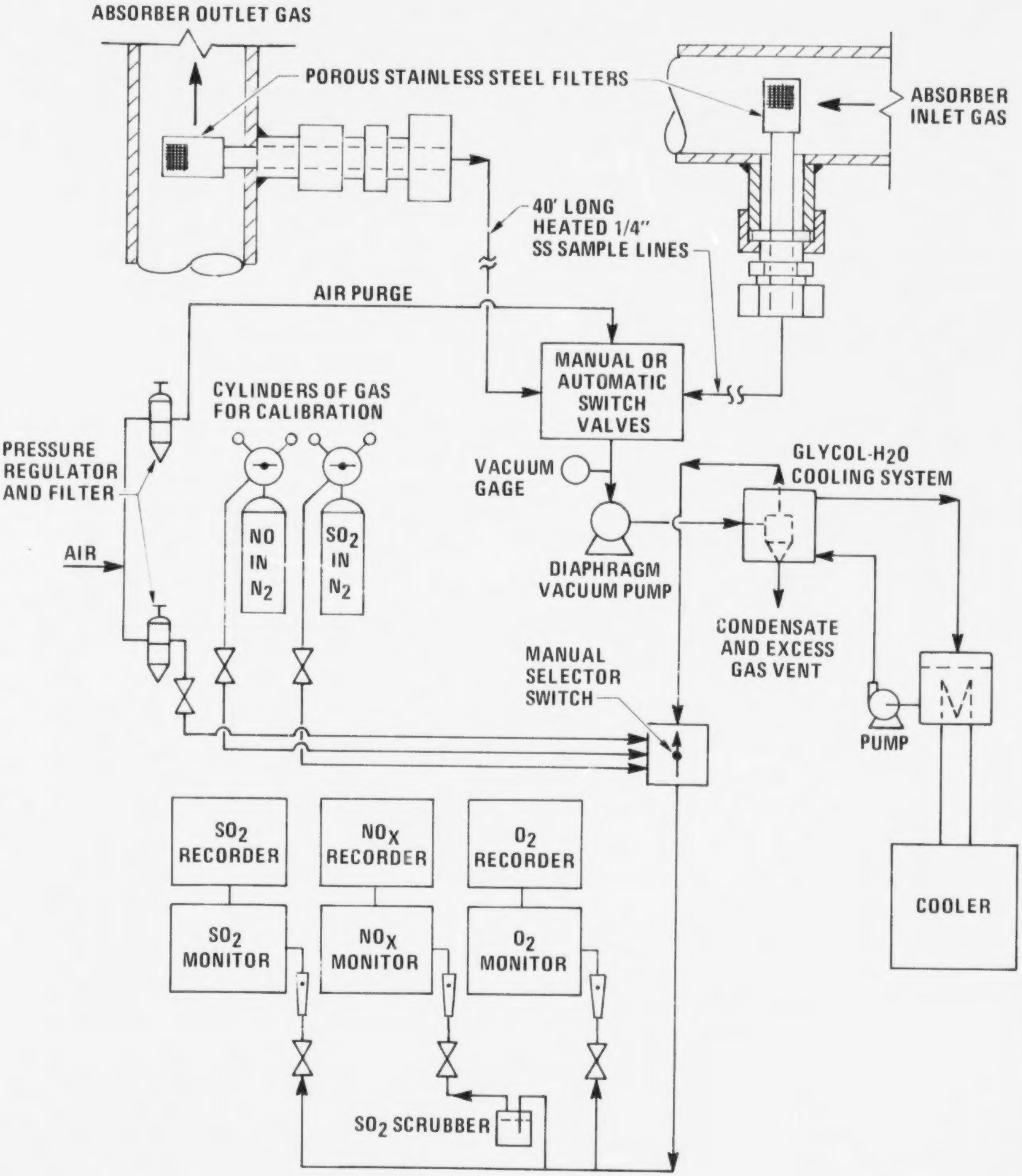


FIGURE 5

SYSTEM I-CALCIUM ABSORPTION

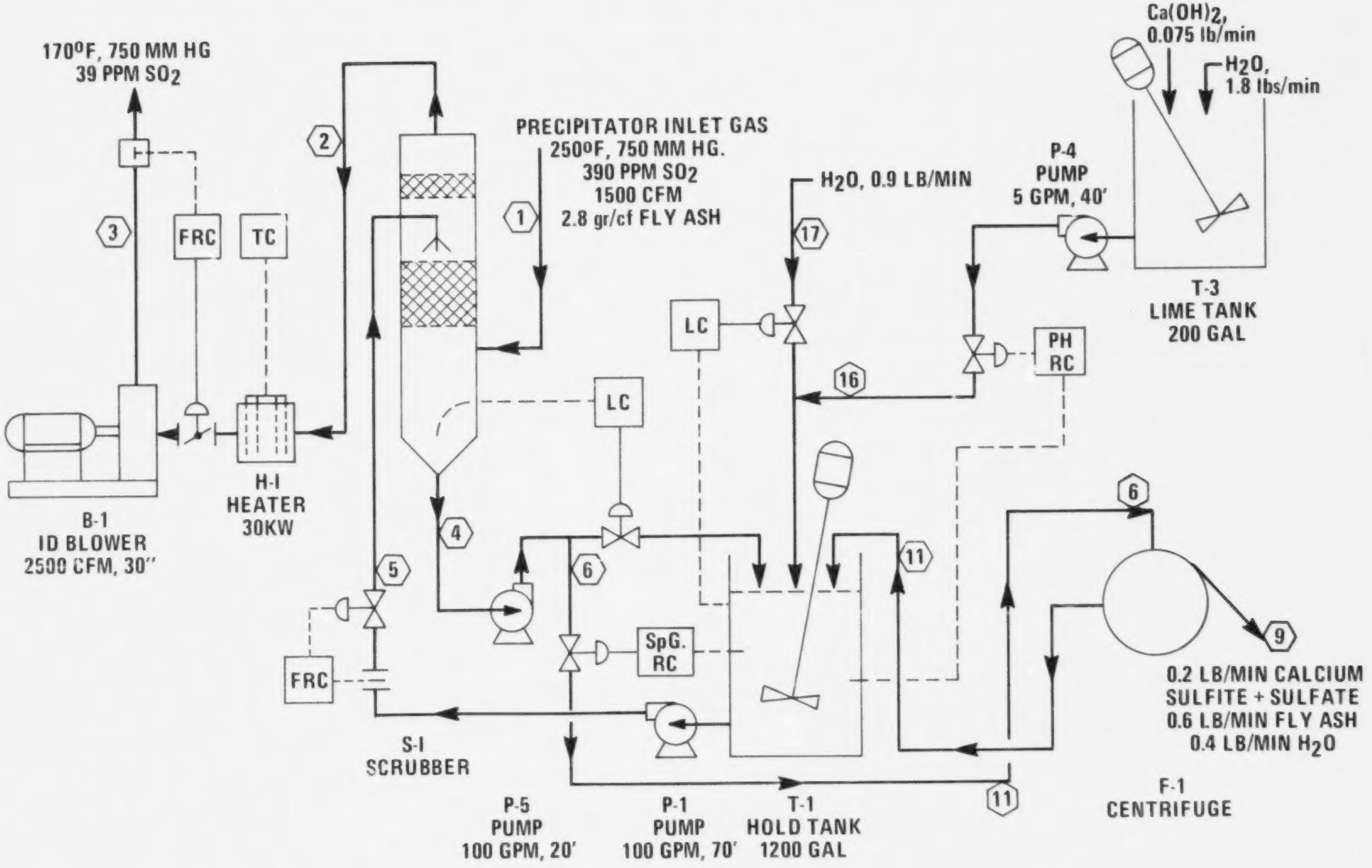
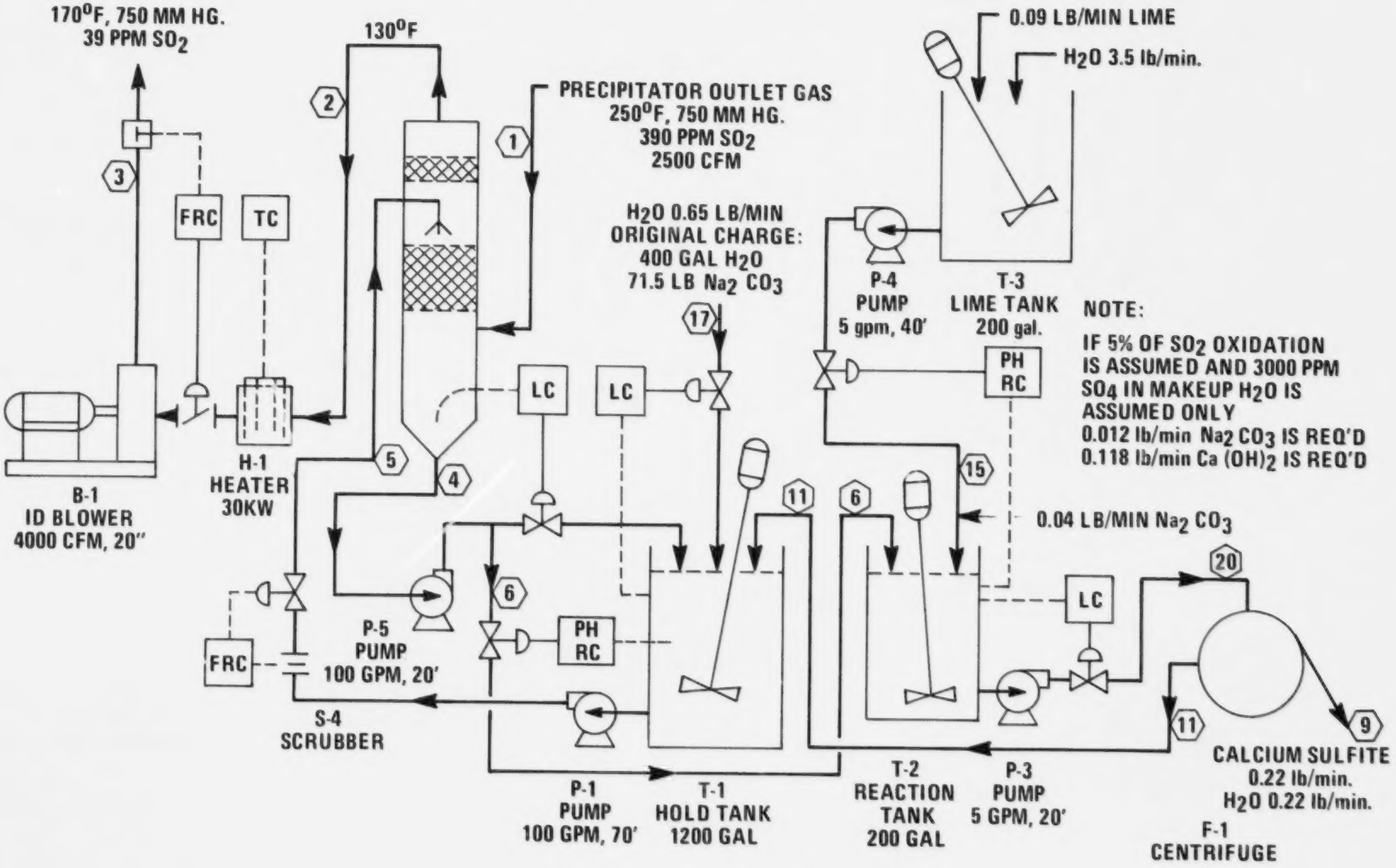


FIGURE 6

SYSTEM II - SODIUM ABSORPTION



NOTE:

IF 5% OF SO_2 OXIDATION IS ASSUMED AND 3000 PPM SO_4 IN MAKEUP H_2O IS ASSUMED ONLY
0.012 lb/min Na_2CO_3 IS REQ'D
0.118 lb/min $Ca(OH)_2$ IS REQ'D

DETROIT EDISON PILOT PLANT AND FULL-SCALE DEVELOPMENT PROGRAM FOR ALKALI SCRUBBING SYSTEMS - A PROGRESS REPORT

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For presentation at the Second International Symposium on Lime and Limestone Wet Scrubbing Sponsored by Environmental Protection Agency, Office of Air Programs, Division of Control Systems

Detroit Edison Pilot Plant and Full-Scale Development Program for Alkali Scrubbing Systems-- A Progress Report

This paper includes the material which was originally to be presented in two separate papers--4c, "Detroit Edison Pilot Plant for Alkali Scrubbing Systems" and 7c, "Detroit Edison Full-Scale Development Program for Alkali Scrubbing Systems." The text of Paper No. 7c is not included in this proceedings.

DETROIT EDISON PILOT PLANT AND FULL-SCALE DEVELOPMENT PROGRAM FOR ALKALI SCRUBBING SYSTEMS - A PROGRESS REPORT

ABSTRACT

In September, 1970, The Detroit Edison Company announced its plans to construct a full-scale limestone scrubbing system for control of sulfur oxides on its 280 megawatt River Rouge Unit No. 1. At that time, and of this date, there is no commercially proven system utilizing limestone for scrubbing in operation. Proven commercial sulfur oxide control systems for the utility industry are ones that: 1) can be ordered from a manufacturer as we do with a boiler, 2) can be installed in a coal burning plant with a reasonable construction time and cost, 3) can be started up and operated with a high degree of service reliability so that sulfur oxide is controlled the majority of the time that the generating unit is running and, 4) incorporate a practical method of handling and disposing of large quantities of waste materials. The River Rouge project is considered a research and development program. The Detroit Edison Company developed a pilot plant program which would provide for the detailed examination of the sensitivity of a sulfur oxide removal system to variations in the different process parameters. This paper describes the basis for formulation of the pilot plant program, how the pilot plant results must relate to the design and selection of equipment for the full-scale installation, and preliminary results of several investigations carried out in the pilot plant to date.

The specific objective of the pilot plant program is to study, evaluate, and demonstrate the system behavior with respect to: 1) level of sulfur dioxide removal from the flue gas, 2) level of entrainment and outlet particulates in the flue gas leaving the scrubbing system, 3) sensitivity of the system to turn down in the flue gas rates, 4) short-term scaling and solids deposition problems, 5) mechanical problems related to equipment and operation, 6) the effectiveness of lime, limestone, and other available alkalis.

INTRODUCTION

The Detroit Edison Company has announced plans to construct a full-scale limestone scrubbing system for control of sulfur dioxide on its 280 megawatt, River Rouge Unit No. 1. The steam generator of this unit has a front-fired pulverized fuel furnace that is equipped with mechanical cyclone separators followed by electrostatic precipitators. When constructed in 1956, these devices represented the latest in particulate emission control technology. However, more restrictive air pollution codes indicated the need for upgrading the collection equipment. Various alternatives for upgrading the performance of equipment at the plant were explored. Among the alternatives was the addition of a wet scrubbing device after existing equipment.

Impending regulations on emission of sulfur oxides indicated that fly ash control systems should not be considered independent of sulfur oxide control, even though the latter had not been commercially proven. Therefore, it was decided that scrubbers should be installed since they would also provide for SO_2 control. Proven commercial sulfur oxide control systems for the utility industry are ones that: 1) can be ordered from a manufacturer as we do with a boiler, 2) can be installed in a coal burning plant with a reasonable construction time and cost, 3) can be started up and operated with a high degree of service reliability so that sulfur oxide is controlled the majority of the time that the generating unit is running and, 4) incorporate a practical method of handling and disposing of large quantities of waste materials. Examination of available information on sulfur oxide control and work that had been done from the 1930's to now, indicated that the most promising concept for add-on systems to existing units was the limestone wet scrubbing system. The major factors favoring the use of limestone in such a system, at this time, are the low cost and wide availability of limestone, apparent simplicity relative to sulfur recovery systems, and minimum potential for water pollution problems.

RIVER ROUGE SCRUBBER PROJECT

The River Rouge project is considered a research and development program. Because of the lack of demonstrated performance of full-scale systems and the variety of scrubber designs, it was decided that this project would include a pilot scrubber installation as well as a full-scale alkali scrubbing system. This parallel approach was needed for the following reasons.

1. Specific pilot plant data concerning performance of various scrubber designs and the process chemistry of these systems were not available.
2. System reliability in terms of equipment dependability and operating efficiencies were not known.
3. Criteria regarding the effectiveness of different limestones had not been adequately established.
4. Actual costs as quoted by equipment suppliers bidding to specifications were not available.
5. Physical and chemical characteristics of waste products, with regard to water pollution potential and solid waste disposal methods, required further identification.
6. Operating experience with this type of equipment had to be acquired.

Bechtel Corporation is designing the full-scale limestone scrubbing system for River Rouge Unit No. 1, and participating in Detroit Edison's pilot scrubber program.

PILOT PLANT PROGRAM

In order to accomplish the objectives outlined above, a pilot scrubbing installation capable of handling up to 2500 ACFM of flue gas from an operating power boiler was constructed at the River Rouge Plant. The pilot program was designed to examine the following:

1. Level of sulfur dioxide removal from flue gas.
2. Levels of entrainment and outlet particulates in flue gas leaving the scrubbing system.
3. The sensitivity of the system to turn down in flue gas rates
4. Short-term scaling and solids deposition problems.

5. Mechanical problems related to equipment and operation.
6. The relative effectiveness of various alkalis such as limestone, lime, and others.

In order to minimize the number of limestones that would have to be evaluated in the pilot plant, laboratory screening tests were carried out. The reactivity of available stones was compared with that of reagent grade calcium carbonate from two different sources. Results indicated that Presque Isle and Rogers City limestones were comparable with regard to reactivity. Arrangements were made to have a supply of Presque Isle limestone ground to various degrees of fineness, bagged, and shipped to the pilot plant. The chemical and physical characteristics of the limestone are given in Table I. Included also are typical coal and ash analyses for the unit supplying flue gas to the pilot plant.

The physical arrangement provides the flexibility to study several different types of scrubbers with minimum system modifications. The scrubber types to be evaluated were: 1) a series of two venturis, 2) a venturi followed by a sieve tray absorber and, 3) a venturi followed by a mobile bed absorber.

Series of Two Venturis

A schematic of the pilot scrubber system employing two venturis is shown in Figure 1. The piping system was arranged so that gas could be taken from either before or after the precipitators of the No. 3 Unit at the River Rouge Plant. After the two scrubbers, the gas flows through a metering orifice and an induced draft fan to heaters which reheat the clean gas to approximately 200 F before it is emitted to the atmosphere. As can be seen in Figure 1, the slurry system is the most complex part of the pilot plant. The slurry is prepared by mixing limestone with clarified liquid from the sludge thickener in a slurry mixing tank. Bagged limestone in various degrees of fineness are available. From the mixing tank, the slurry of alkali scrubbing material is transferred to a large agitated holding tank from which it is metered to the second-stage recycle tank. Slurry is pumped from this tank to the second-stage scrubber at a rate to satisfy a specific liquid to gas (L/G) ratio. A portion of the solution from the second-stage recycle tank is bled to the first-stage recycle tank. Solution from this tank is circulated through the first-stage venturi to satisfy a specific L/G. A portion of the slurry from the first-stage recycle tank is bled to the sludge thickener. Clarified liquid is pumped to the slurry mixing tank. Underflow from the thickener, spent slurry and fly ash, is removed to the plant ash handling system.

A typical operation of this pilot plant arrangement consisted of:

1. Preparing a mixture of slurry in the large mixing tank and filling the recycle tanks to a predetermined level.
2. Establishing gas flow and monitoring inlet temperatures until a constant value is obtained.
3. Starting the recycle pumps at a high rate.
4. Monitoring ph of the slurry until it reaches a level of approximately 6.0.
5. Adjusting slurry recycle to satisfy preselected L/Gs.

Pressure readings, temperature, and sulfur dioxide concentrations are taken at frequent intervals. The instrumentation to make these measurements is installed in a small laboratory that has been built adjacent to the pilot plant. Samples of limestone slurry are taken from the slurry mixing tank and analyzed for calcium carbonate content. With these measurements, the amount of limestone slurry needed to meet a specific stoichiometric value is determined. The slurry feed and discharge rate are then adjusted as needed. Similarly, the L/G is adjusted to meet a predetermined value by holding the gas rate constant and monitoring the liquid flow using magnetic flow meters. The ph of the recirculating solutions is monitored in both the recycle tanks to control scaling in the scrubber and to determine the correlation between ph and SO_2 removal. Suspended solids are measured at the inlet and outlet of the thickener to determine its efficiency.

The results of investigations conducted employing a system of two venturi scrubbers indicate that outlet dust loadings of less than 0.02 grains per standard cubic foot of gas can be achieved. This performance, however, has yet to be adequately demonstrated on a full scale unit. This system has been operated for up to 120 hours without serious plugging or scaling problems. During this series of tests, the system removed from 55 to 65 percent of inlet SO_2, independent of the ratio of excess limestone to sulfur dioxide. The optimum removal efficiencies during these investigations were obtained with liquid to gas ratios between 30 and 40 gallons per minute per 1000 cfm. When the same system was operated with 20 percent excess hydrated lime, greater than 90 percent of sulfur dioxide was removed. These results indicated that, in the case of a venturi scrubber, there is little internal circulation within the drops; consequently, relatively insoluble alkalis such as limestone do not readily dissolve and react with sulfur dioxide which comes in contact with them for short periods of time. On the other hand, the large number of small droplets and large amounts of surface area produced in these units provide for excellent particulate removal.

Venturi Followed by Sieve Tray Absorber

A schematic of the pilot system employing a venturi followed by a sieve tray absorber is shown in Figure 2. In this system, the alkali scrubbing material is transferred from the slurry mixing tank to the large agitated holding tank from which it is metered to the tray absorber feed tank. The slurry is then metered to the absorber section of the scrubber. The limestone slurry then cascades over several stages of trays and flows back to a recycle tank. Solution from the recycle tank is metered to the venturi section of the scrubber. A portion of the solution in the recycle tank is pumped to the sludge thickener. As with the previous system, the clarified liquid is returned to the slurry mixing tank for preparation of new scrubbing solution. Sludge from the bottom of the thickener is removed to the plant's ash handling equipment as with the previous system.

To date, typical operation of this installation has consisted of:

1. Preparing a batch of scrubbing slurry in the mixing tank.
2. Filling the slurry holding tank, absorber feed tank, and recycle tank to a predetermined level.
3. Establishing a flow through the venturi section at a predetermined L/G.
4. Establishing gas flow through the unit, and immediately thereafter, a flow of scrubbing liquid to the absorber section.
5. Adjusting the rate of flow to the absorber section at a predetermined L/G.

Limited experience with this system to date indicates that outlet dust loadings of less than 0.015 grains per standard cubic foot of gas can be achieved. It should be noted, however, that these results represent the performance of a 1/200th scale of the River Rouge unit. Difficulties have been encountered to date in establishing a ph level high enough to control scaling due to precipitation of dissolved solids in the absorber section of the scrubber system. In order to provide more precise ph control, modifications are presently being made to the recycle and alkali feed systems of the pilot plant. As of this writing, significant sulfur oxide removal data have not been obtained.

Operating experience to date has indicated that it is extremely important to have an on-site capability for performing chemical analyses. This has been found necessary because certain parameters must be monitored and the results of that monitoring fed back into the operation of the scrubber in order to examine such characteristics as scaling and deposition potential. This is particularly true in establishing the degree of supersaturation in the supernatant from the sludge thickener.

For each test series, the pilot plant is manned for 24-hour per day operation. On each 12-hour shift, a crew of three men is employed. This crew is composed of an operator from the power plant, a chemical engineer, and an engineering technician who has been trained in chemical analysis. Recently, an analytical chemist has been added to the staff during the day time part of the operation.

Future Plans

Beyond the present test series, it is planned to study the effectiveness of other alkalis including certain chemical process waste products available locally. Of equal importance to the effectiveness of the systems in removing SO_2 are solutions to the waste disposal problems. Therefore, a concurrent program, utilizing waste materials generated by the pilot plant, is underway. This effort includes the development of practical means of handling, transporting, and ultimately disposing of the sludge.

As mentioned earlier, engineering of a full-scale limestone scrubbing system for River Rouge No. 1 is proceeding in parallel with the pilot program. The ultimate configuration of this unit and its operational schedule is dependent upon the outcome of the present pilot program. The current schedule for completion of the full-scale scrubbing system is January 1973.

TABLE I

CHEMICAL AND PHYSICAL PROPERTIES OF LIMESTONE, COAL, AND ASH DETROIT EDISON PILOT SCRUBBER PROGRAM

Presque Isle Limestone

	Silica SiO_2	Iron Oxide Fe_2O_3	Calcium Oxide, CaO	Magnesium Oxide MgO	Sulfur (SO_3)	Loss on Ignition
Percent by Weight	0.60	0.35	54.5	0.60	0.085	43.82

Calcium Carbonate, percent 97.5
Magnesium Carbonate, percent 2.5

Coal

	Volatile Matter	Moisture As Fired	Ash	Sulfur	Total Carbon	Hydrogen	Nitrogen	Oxygen
Percent by Weight	36	6.3	12	2.8	72	4.8	1.7	5.5

Fusion temp (fluid) - 2350 F Heating Value - 12000 BTU/lb.

Ash

	Loss on Ignition	Silica SiO_2	Iron Oxide Fe_2O_3	Alumina Al_2O_3	Calcium Ca O	Magnesia MgO	Titanium TiO_2	Sodium Na_2O	Potassium K_2O	Carbon C	Sulfur SO_3
Percent by Weight	3.4	40	30	17	2.6	0.6	0.9	0.3	1.8	2.9	1.1

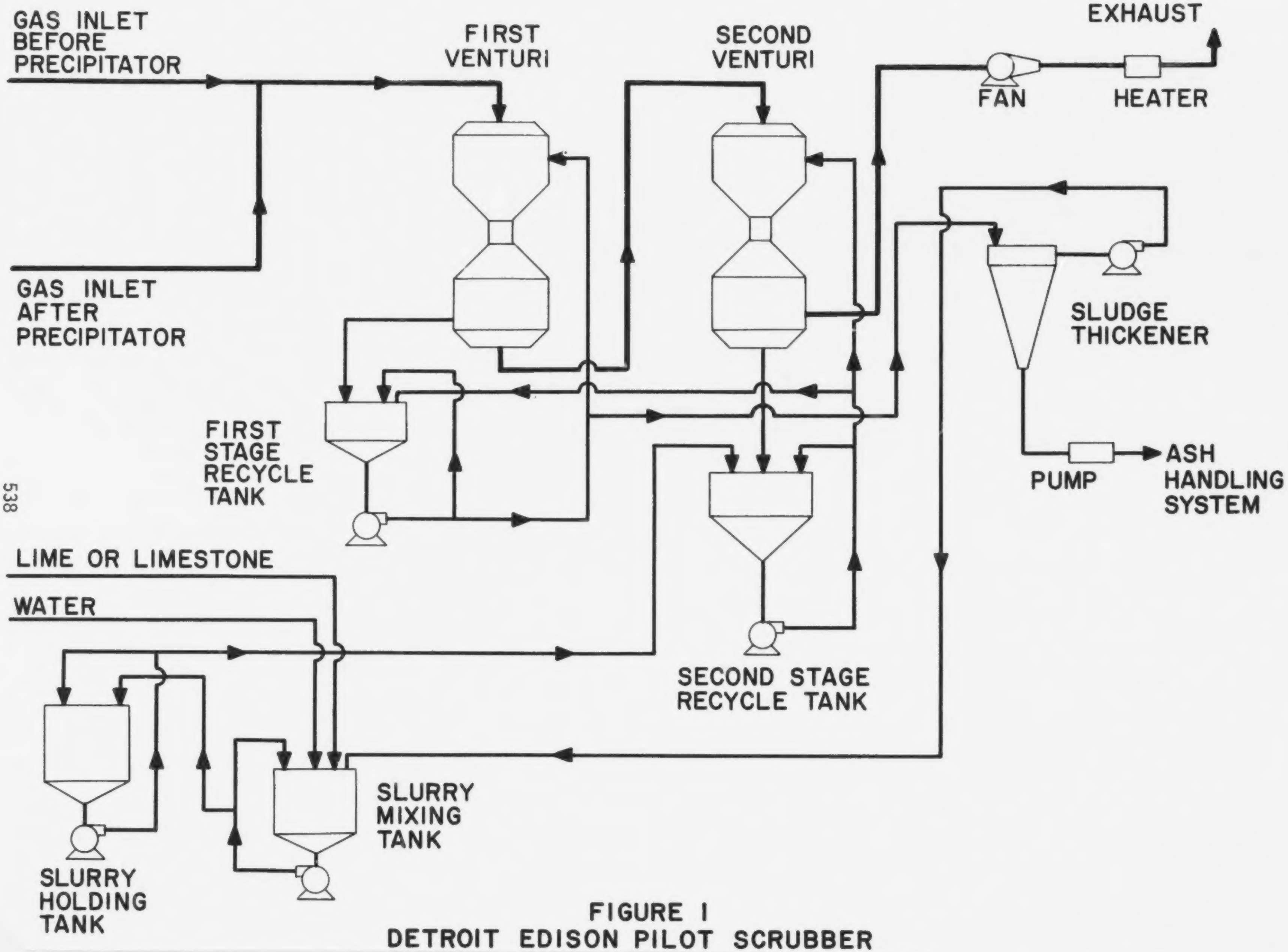

FIGURE I
DETROIT EDISON PILOT SCRUBBER

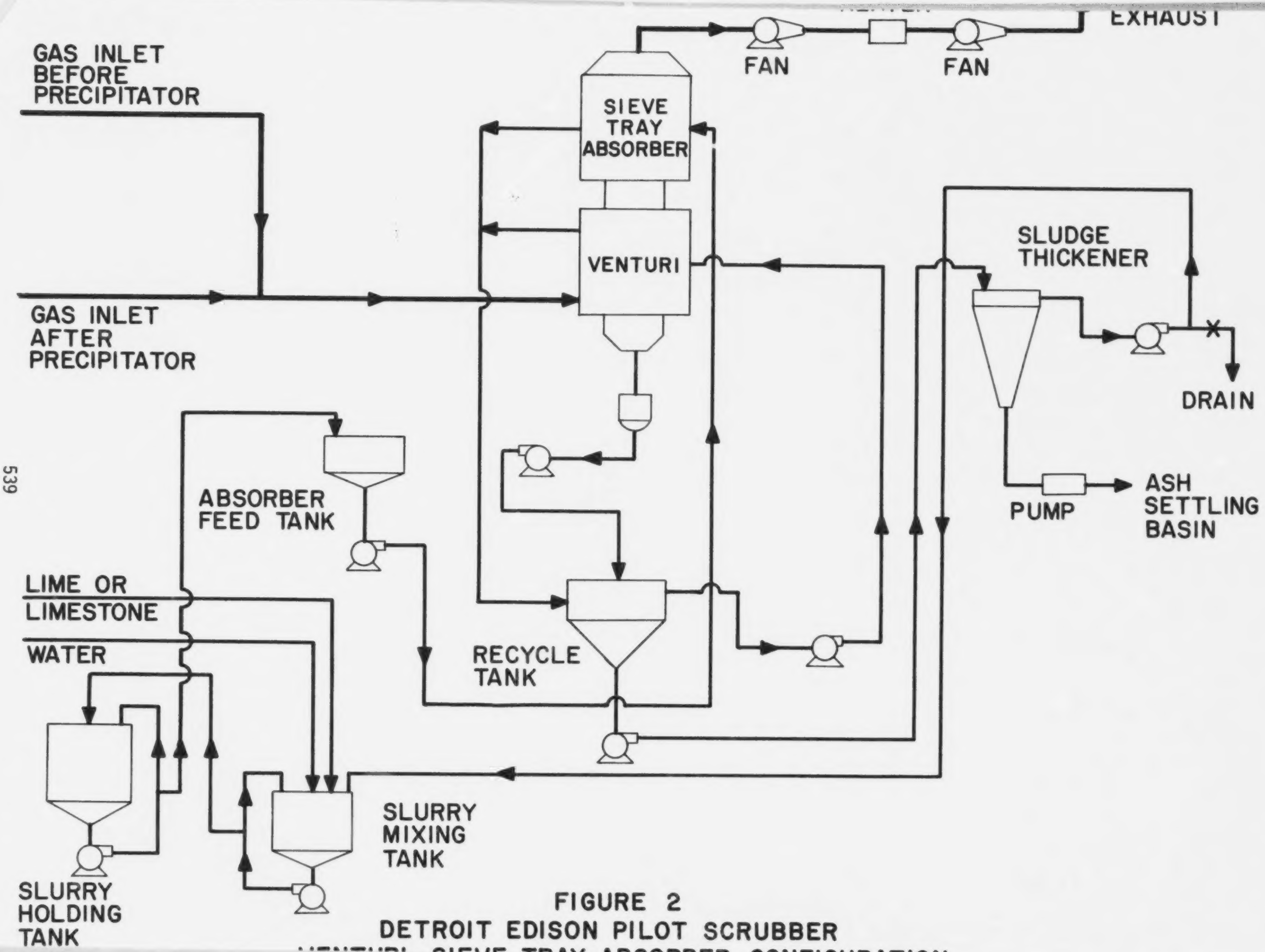

FIGURE 2
DETROIT EDISON PILOT SCRUBBER
VENTURI SIEVE TRAY ABSORBER CONFIGURATION

RESEARCH & DEVELOPMENT IN WET SCRUBBER SYSTEMS

by

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Presented at

SECOND INTERNATIONAL LIME/LIMESTONE WET SCRUBBING SYMPOSIUM

November 8-12, 1971

Sheraton-Charles Hotel, New Orleans, Louisiana

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RESEARCH & DEVELOPMENT IN WET SCRUBBER SYSTEMS

A. L. Plumley

and

M. R. Gogineni

The subject of this paper is the research and development supporting Combustion Engineering's product line of air pollution control and by-product recovery systems to meet Federal standards for air and water pollution. Major emphasis of this program centers on providing design criteria and engineering support for commercial systems.

R&PD PROGRAM OBJECTIVES

The following have been established as both short and long range objectives of C-E Research and Development Program for Air Pollution Control Systems:

A. Complete development of limestone furnace injection demonstration systems to meet contract obligations for SO_2 and particulate removal.

B. Establish design criteria for future systems at lower cost using the present APCS principles.

C. Develop non-furnace injection systems for both utility and industrial boiler applications.

D. Develop improved air pollution control systems to reduce other air pollutants and to allow expansion of a company product line.

E. Develop by-product utilization processes to avoid potential water and land contamination and to offset operating costs of current and future air pollution systems.

The R&D program is divided into two principle areas of effort:

1. Air Pollution Control Systems Development
2. Chemical Process Research

AIR POLLUTION CONTROL SYSTEMS DEVELOPMENT

Air Pollution Control Systems Development is comprised of performance work on full scale systems in the field and experimental work done on our test facilities in the laboratory. Design criteria are confirmed in this area of development.

The first area of development involves the APCS contracts which C-E has obtained. These contracts are listed and described in another paper at this conference, entitled "Contract Applications of the C-E Air Pollution Control Systems".

The second area of Air Pollution Control Systems Development is comprised of all the experimental work done in the laboratory on our scrubber test facilities. There are two operating APCS test facilities available in the Kreisinger Development Laboratory for evaluation of wet scrubber technology: A 12,000 CFM Prototype system and a 1,200 Pilot system (Figures 1 to 4).

These APCS test facilities are comprised of all system components utilized by the existing C-E installations and are assembled in a modular arrangement to allow rapid system modifications. In this way, a number of flow arrangements can be studied.

CHEMICAL PROCESS RESEARCH

The Chemical Process Research section is concerned with two major areas. The first is the fundamental understanding of reaction mechanisms associated with our wet scrubber work and the second is the disposal of waste materials from APCS operations. The more fundamental work is carried out in various types of laboratory bench reactors and is designed primarily to provide supplementary information to the larger scale test facilities and to screen variables to be evaluated during pilot and prototype tests.

As the overall program develops, co-ordination of various technologies related to environmental control, both solid and liquid wastes, as well as air pollutants, will be carried out.

TEST WORK

Test work is currently underway which is directed at providing sufficient design information to resolve problems remaining on the demonstration field installations thus allowing them to meet contract guarantees as well as federal and local regulations on SO_2 and particulate removal. Field development is expensive and time consuming since generation of power takes precedence over the check-out of field modifications and other work necessary in evaluation of new processes and new process development. We have experienced considerable time, months of delay, between modifications and their evaluation in these field systems. As a result, most of our development work is being carried out on the two operating APCS test facilities in the laboratory.

Prototype (Figures 1 and 2)

The APCS prototype is approximately 1/4 the linear scale of C-E's field units and utilizes a 25 sq. ft. marble bed contactor to scrub the flue gases from the oil fired packaged boiler. This boiler has a flue gas output of 12,500 to 15,000 ACFM measured at 14.7 psia in

125°F. The inlet gas temperature to the scrubber is variable; the 600°F flue gas from the boiler can be reduced to 250°F by means of a finned tube heat extractor prior to the scrubber.

Major components of the system are the scrubber, heat extractor, reheater, demister, clarifier or retention tank, and the slurry or hold tank with provisions for additive and fly ash injection. The piping and pumps can be readily modified to allow study of several different processing arrangements.

Pilot (Figures 3 and 4)

The APCS pilot system features multiple three sq. ft. marble beds, as well as 1 sq. ft. rod type contacting surfaces which may be operated in various combinations to determine the most effective use of additives for SO_2 removal from flue gas. Provision has been made for evaluation of other types of scrubbing surfaces. Separate collection of particulate and SO_2 is also possible in this system. The major system components in addition to the scrubber with its multiple beds are the demister, clarifier, slurry and delay tanks additive and fly ash injection systems. Here, too, piping and pumps can be modified to allow several different processing arrangements. The system is currently being used to carry out preliminary screening of variables so that only optimum modes will be demonstrated on the prototype proper.

Bench Scale Facilities

There are three principal bench scale facilities that are utilized in the APCS studies. In general, the purpose is not to perfectly scale down APCS either from field or laboratory, but to provide small flexible laboratory tools in which to study various phenomenon including packed-bed mass transfer rates, scaling phenomena and rates of reaction to provide a basis for correcting certain problem areas observed in operation of either the larger scale laboratory or field facility. The first of these facilities, the bench scale scrubber, is a tube which has been flanged and divided into three sections (See Figures 5 and 6). The lower section contains a gas inlet in the liquid drain, the middle section contains the bed, the nozzle and the bed drain, and the upper section contains the mist eliminating section and the gas outlet. These sections are removable for modifications and repairs. The rest of the apparatus is concerned with controlling concentration, temperature and flowrates of reactants. Instrumentation includes temperature controllers, SO_2 monitors, temperature monitors, and the pH meters.

The next type of facilities are stirred reactors. We have a CFSTR or Continuous Flow Stirred Tank Reactor. This equipment is used to understand scrubber reaction kinetics by direct determination of differential rate data for the various reactions taking place in the scrubber. This is important in design of system controls as well as in sizing of system components. In this reactor the contents are well stirred and uniform in composition throughout. Thus, the exit stream from this reactor has the same composition as the fluid within the reactor and analytical results on this stream represent the behavior of the system.

The second type of stirred reactors are batch type reactors. These consist of a pair of temperature controlled flasks. System reactions, specifically those relating to potential deposit formation, and for preparation of scrubbing solutions, delay tanks, holding tanks, etc. are being studied. (Figure 7)

The holding effects of ponds to allow for completion of reactions including precipitation of solids and dissolution of potential reacting materials which are being recirculated in the overall system are being simulated in bench tanks.

CHEMICAL PROCESS DEVELOPMENT

WASTE DISPOSAL

A comprehensive program for utilization of APCS by-products is currently underway. This six phase program covers:

1. Nationwide environmental survey of present waste disposal procedures and ecological data relating to the needs of potential APCS customers.
2. Determination of physical and chemical properties of waste products.
3. Studies on direct disposal of both solid and liquid wastes.
4. Beneficiation and utilization of liquid and solid waste products.
5. Pilot plant studies of promising utilization of procedures.
6. Economic and technical summary and recommendations.

A significant part of the understanding of physical and chemical properties is being carried out with the assistance of C-E's modern X-ray diffraction and X-ray spectrographic equipment and recently acquired thermal analysis equipment. This instrument (Figure 8) is capable of performing simultaneously the three most widely used thermoanalytical techniques: Differential Thermal Analysis (DTA), Thermal Gravimetric Analysis (TGA) and Differential Thermogravimetric Analysis (DTGA).

The instrument has been utilized so far in determination of melting point, decomposition temperature and sinterability of waste sludge from APCS operations (Figure 9). These are all properties needed for determination of appropriate utilization applications of the material.

Characterization

Work is underway on development of a sludge "library" by cataloging of ten different chemical and physical properties of sludges from various APCS operations in both field and laboratory studies. This information is essential since the utilization or disposal process in each instance will depend on both the additive used and the mode of APCS operation. (Figure 9).

A number of areas for utilization of modified and unmodified fly ash are shown in Figures 10 and 11. These schemes range from production of light weight aggregate developed some years ago to compression and sintering of drain pipes which is under laboratory development. Large volume usage will be necessary since 1-2 tons/day/MW of sludge would be produced from a coal-fired boiler firing 3% S coal and 10% ash with an APCS for emission control.

Beneficiation

A number of small brick and pipes have been successfully produced from APCS sludge by Industrial Material Technology, Inc. Samples formed by high pressure without sintering appeared most promising. Efforts are continuing to improve durability and optimize fabrication methods for large quantity production.

ACRES, Inc. has submitted a proposal to define the geotechnical properties of the APCS sludge. Properties involved are important in designing structural fill - dams, dikes, pavement and other load bearing land-fill usage. ACRES, Inc. has been retained by Niagra Mohawk to handle ash disposal problems.

The evaluation of APCS sludge for hydrothermal bricks is continuing at Michigan Technology University.

Environmental Survey

A report summarizing the results of an environmental survey has been completed. Compilation of current Federal, State and Local pollution codes is continuing.

Direct Disposal

A meeting of the National Ash Association in Washington discussed plans for transportation of fly ash by rail from the utility to the disposal site. It was decided to also include modified fly ash (from lime/limestone wet scrubbing). Representatives of leading coal producers were present to consider use of abondoned mines as disposal sites. No firm decisions were reached.

The EPA Office of Solid Wastes is continuing to evaluate an unsolicited C-E proposal for study of direct disposal procedures for APCS sludge.

BENCH STUDIES

An extensive laboratory investigation designed to reduce the liquid blowdown required to control calcium sulfate (gypsum) deposit formation during APCS operation is underway at KDL. This work is essential to avoid replacing an air pollution problem with water pollution.

The three-point bench study is directed at development of a "closed cycle" system in which the only liquid discharge from the APCS is that conveying solids which can be recycled, thus requiring no blowdown to the river.

The most promising technique resulting from the bench study will be followed by a demonstration run on the 1200 cfm APCS pilot facility.

Other bench scale support studies are underway to provide aid in understanding of scrubber chemistry and mass transfer within the APCS and similar SO_2 removal system. Included are:

A. Reliability of extrapolation of bench units to larger systems.

B. Confirmation of the marble bed as a completely back mixed system as part of fundamental studies on mass transfer within the bed.

C. Basic studies on oxidation of sulfites and the subsequent relationship to both SO_2 absorption in the scrubber and control of both sulfite and sulfate deposit formation.

D. Use of a Continuous Stirred Tank Reactor to aid in equipment sizing by determination of rate controlling steps in various phases of the APCS operation. Dissolution of alkali (CaO and $CaCO_3$) as well as precipitation rate of sulfates and sulfites are under study.

TEST RESULTS

Experimental work since 1970 dealt with specific problems in the field demonstration system. Control drain line scaling and optimization of slurry recycle (both clarifier and scrubber underflow) have been studied.

The under bed addition of slurry and dry injection of additive in the gas stream have given comparable results in both SO_2 removal and chemical efficiency of additive. Both procedures result in passage of both additive and SO_2 through the bed and it may be concluded that the intimate mixing thus achieved is required for maximum efficiency of operation.

SO_2 removal of 90 - 95 percent have been achieved with both dry injection and slurry addition of hydrated dolomite. About 10% more hydrated lime is required than hydrated dolomite to give comparable SO_2 removal.

Experimental work in 1970 on the APCS prototype test facility emphasized optimization of slurry additive or tail-end systems utilizing calcium carbonate as the additive.

In a series of single marble bed tests at 1000 ppm SO_2, 50 to 300% stoichiometric limestone slurry was fed through underbed spray nozzles with no recycle. SO_2 removal ranged from 40 to 75%. The formation of calcium sulfate ($CaSO_4$) deposits in the scrubber, is being controlled by blowdown tests.

Experimental work in 1971 on the Air Pollution Control System (APCS) test facilities has emphasized optimization of tail-end slurry additive systems which can be installed in Unit No. 1 at the Meramec station of Union Electric and Unit 6 at the Paddy's Run Station of Louisville Gas & Electric. Both single and dual marble bed studies have covered use of both calcium carbonate (for Union Electric) and calcium hydroxide (for Louisville) with inlet SO_2 concentrations of 1000 and 2000 ppm.

Following a series of successful pilot and prototype tests extended runs to demonstrate reliability were carried out with dual bed operation and recycle using lime in a scale up of previous pilot studies.

During an 80 hour run with an appropriate recycle of scrubber effluent sulfur removal in excess of 80% was maintained without scaling. Dust loadings at the outlet were about 0.03 gr/SCF.

Louisville Gas & Electric approved construction of a full scale APCS at Paddy's Run Station on the basis of these successful tests.

An extended run to demonstrate reliability was carried out utilizing dual bed operation with maximum recycle of scrubber effluent through the slurry tank using calcium carbonate. This scale up of previous studies extended for 125 hours without deposit formation and resulted in sulfur removal efficiency in excess of 75%.

Laboratory and pilot studies are continuing to understand the overall chemical balance as related to blowdown and waste disposal. Approval of full scale APCS construction is expected in the near future.

EPA CONTRACT FOR RESEARCH IN SCRUBBER TECHNOLOGY

C-E has received its first prime contract from the Office of Air Programs - Environmental Protection Agency (EPA). This $250,000 contract is for the "Optimization of a Lime/Limestone Wet Scrubbing Process for SO_2 and Particulate Removal in a Marble Bed Scrubber.

A general outline of the program is as follows:

Impending national performance standards and standards being set by state and local air pollution control office authorities requires the rapid development of as many SO_2 emission control processes as possible. Several processes are now being developed, including the Combustion Engineering (C-E) Lime/Limestone Wet Scrubbing process, which has been under development for about three years. Two full scale units of this process have been installed on separate 125 MW power plants.

The purpose of this contract is to conduct research and development on small pilot scale, large pilot scale and full plant versions of the C-E SO_2 scrubbing process in order to accelerate its commercial development. Principle capabilities to be developed and demonstrated include adequate SO_2 and particulate removal, proven operational reliability, adequate equipment lifetime, adequate capability for scale-up, and sufficient estimates of process costs.

The following specific work steps are anticipated:

1. Engineering Analysis - Existing C-E data and all related data from other EPA contractors to develop the final test program and calibrate mathematical process model.

2. Soluble System Studies - KDL Prototype determination of the approach to vapor-liquid equilibrium and the mass transfer capabilities of marble bed scrubber and validation of input to mathematical process model using Na_2CO_3 solution.

3. Prototype Test Program - KDL - To provide optimization of the present C-E APCS based on input from 1, 2, and 4.

4. Prototype tests - KDL - Verification of prototype as model for prediction of field unit operation.

5. Prototype Tests - KDL - Final calibration to determine optimum operation for field units.

6. Field tests - to demonstrate on the field units, under a separate contract, the optimum operating conditions determined from the KDL Prototype tests and to arrange for the final confirmation of mathematical process model.

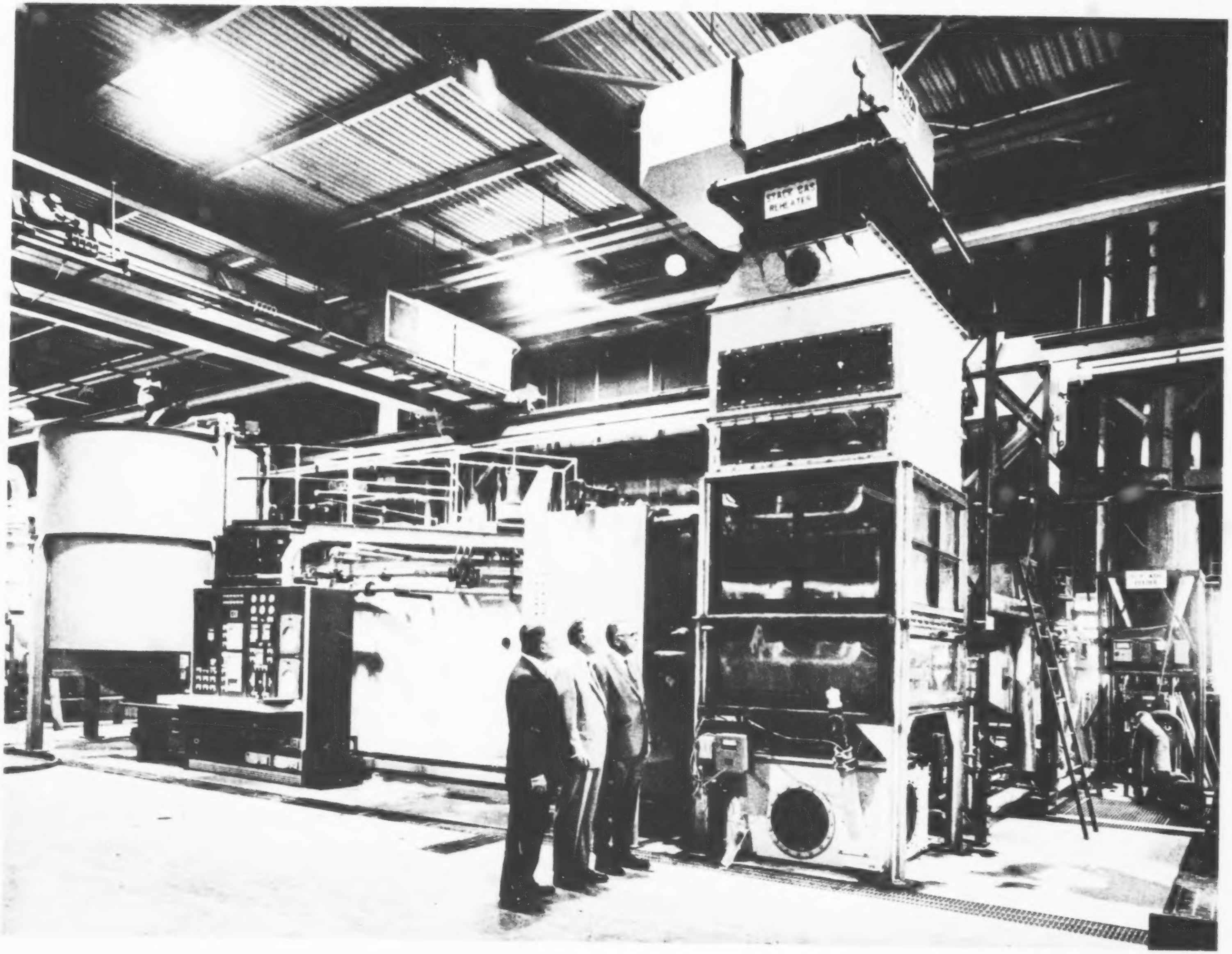
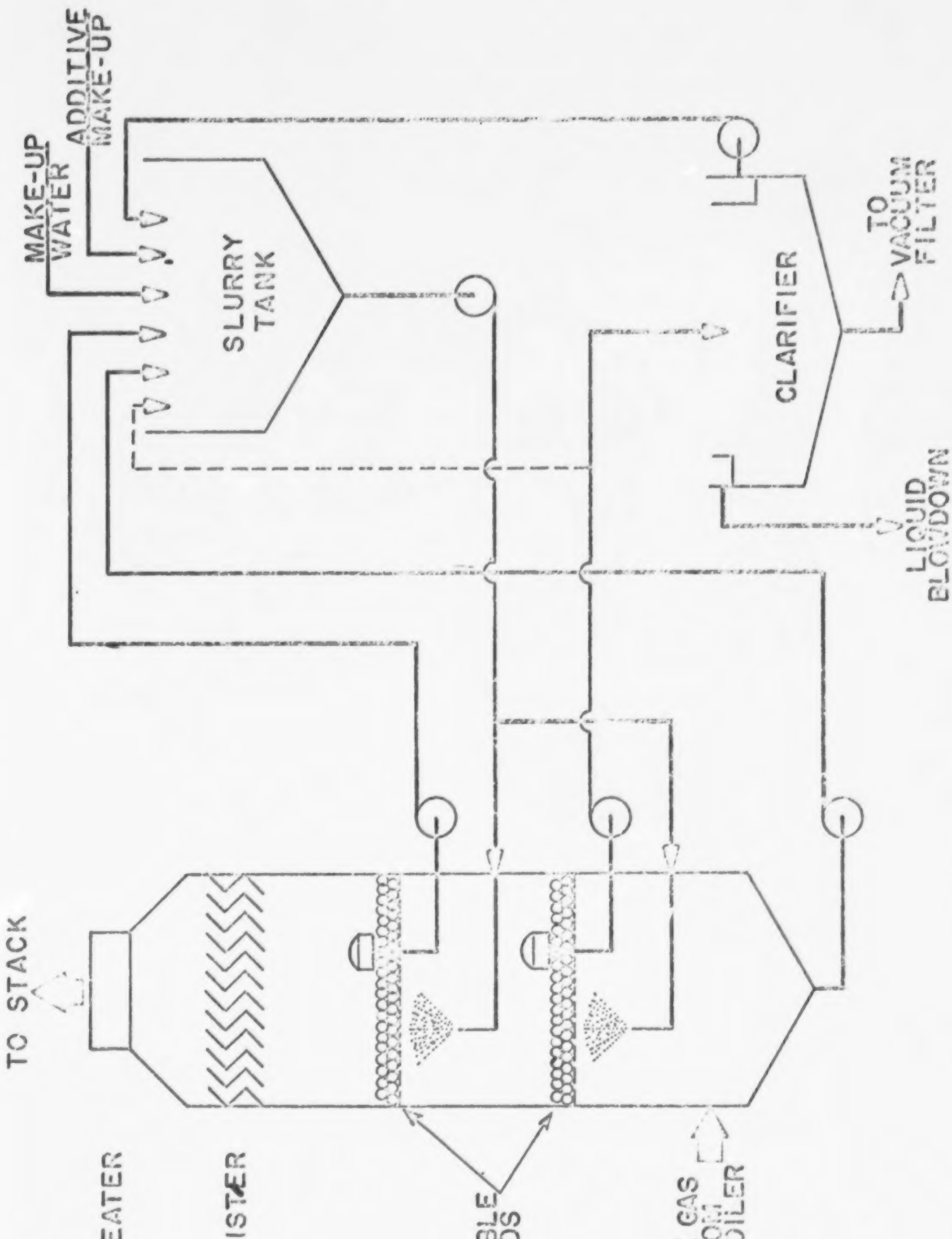


FIGURE -1



APCS PROTOTYPE-TAIL-END SYSTEM

FIGURE 2

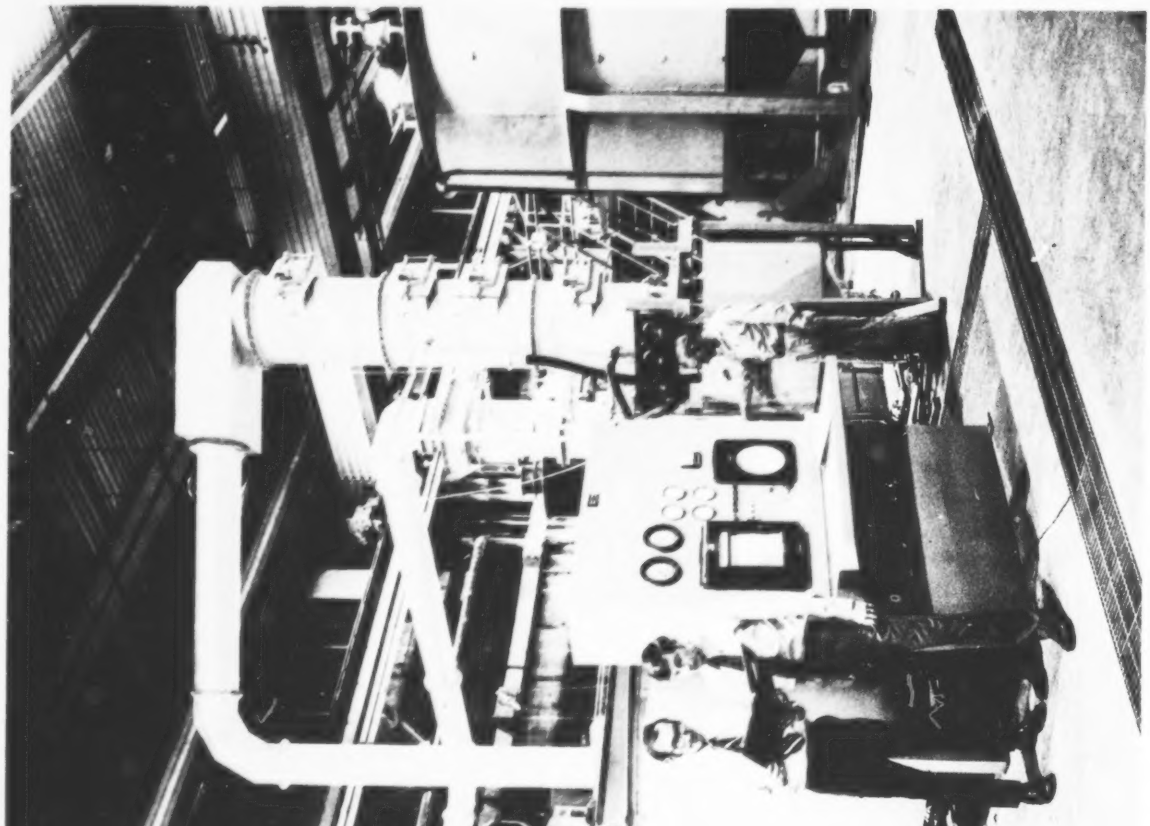


FIGURE -3

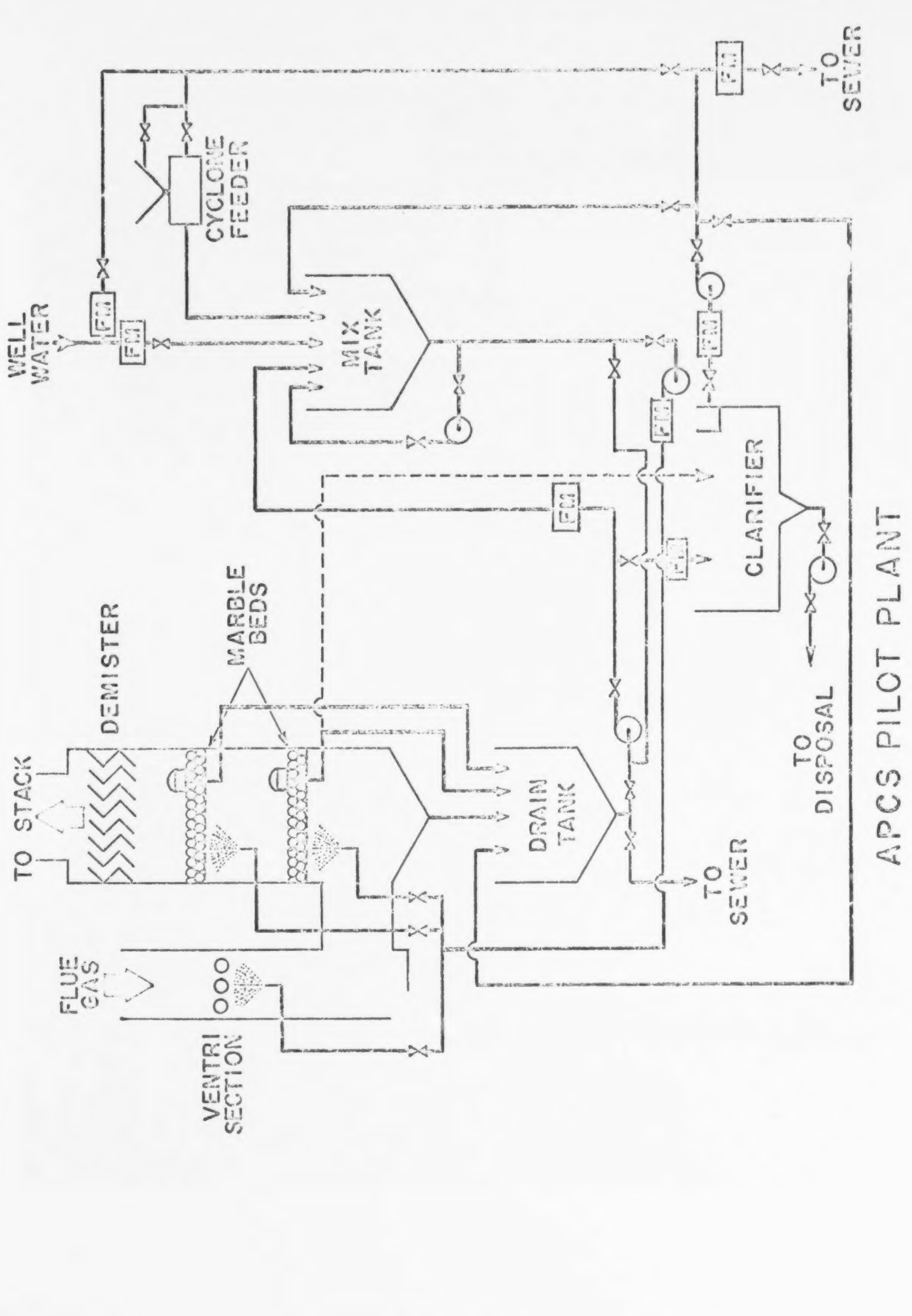

APCS PILOT PLANT
TO STACK
DEMISTER
MARBLE BEDS
FLUE GAS
VENTRI SECTION
DRAIN TANK
TO SEWER
TO DISPOSAL
CLARIFIER
MIX TANK
WELL WATER
FM
CYCLONE FEEDER
TO SEWER

FIGURE -4

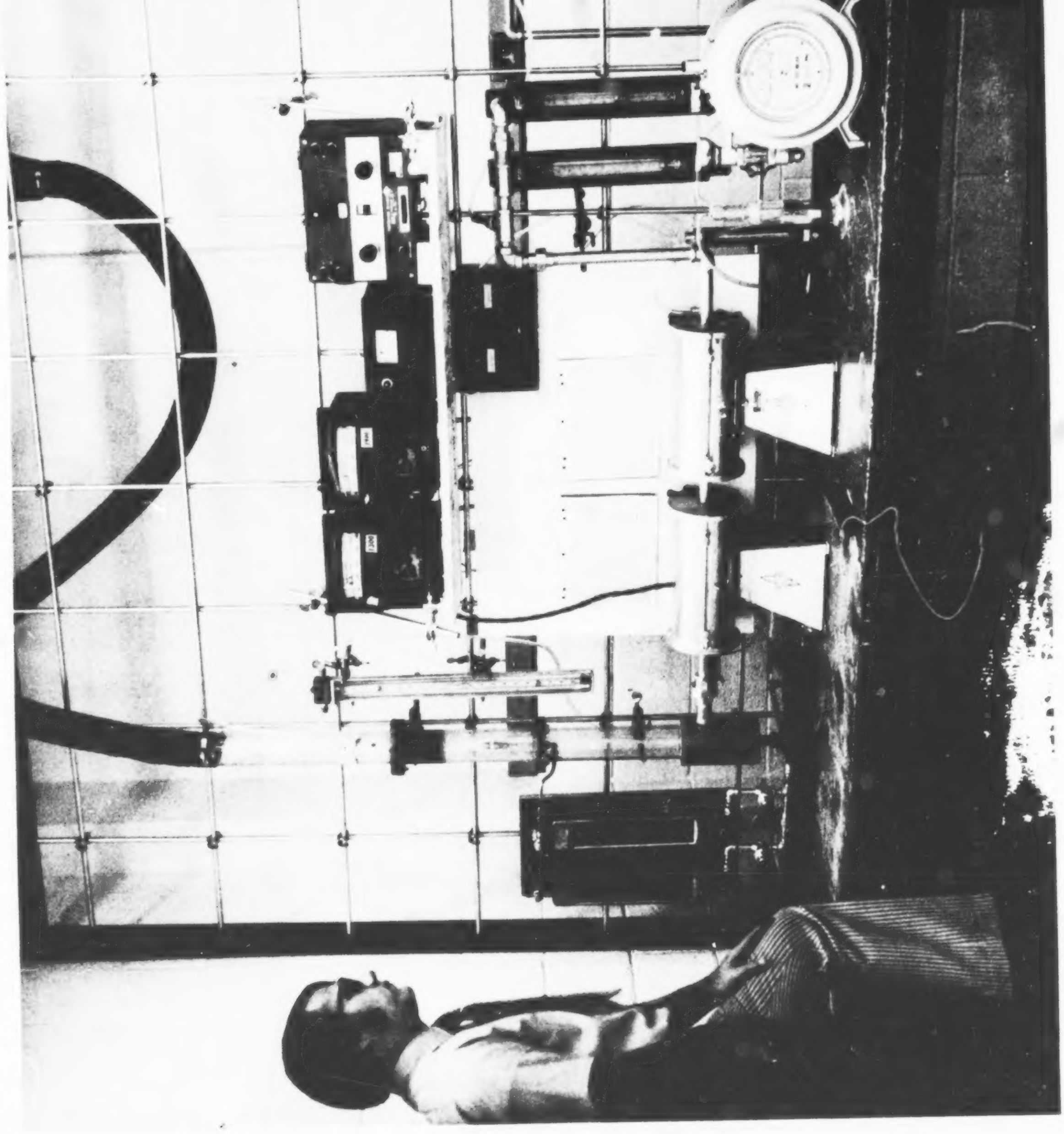
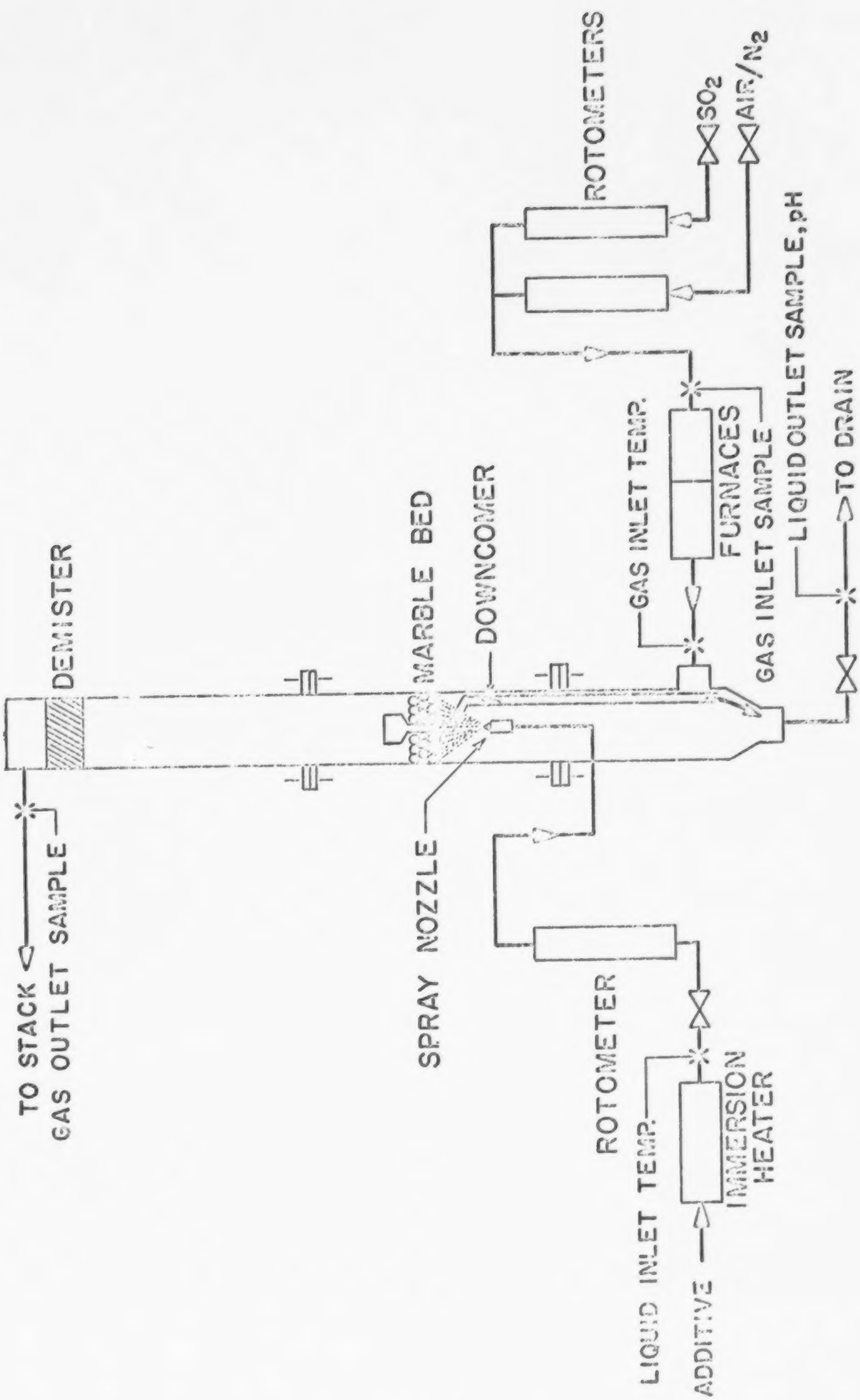


FIGURE -5



SCHEMATIC OF BENCH SCALE SCRUBBER SYSTEM

FIGURE 6

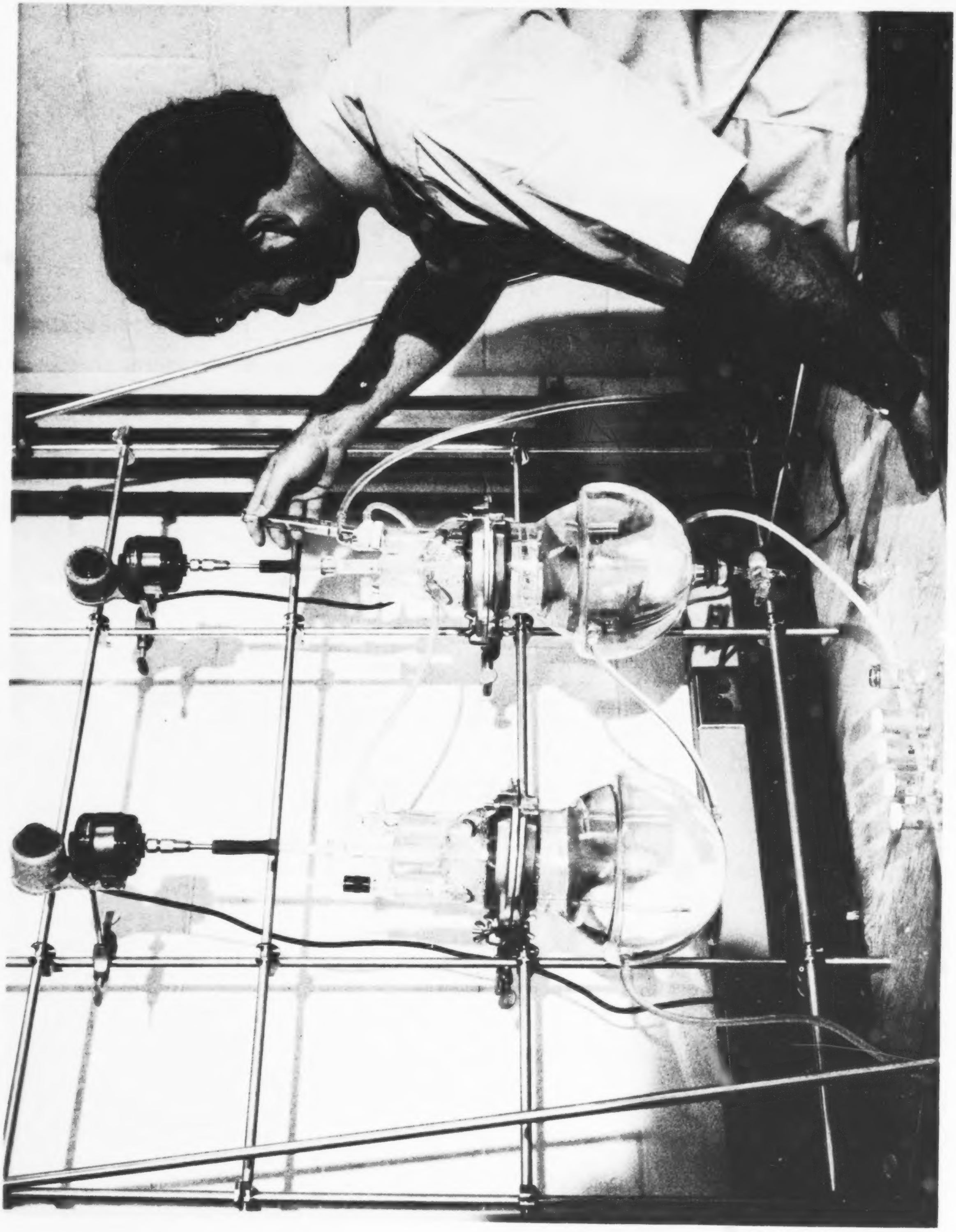
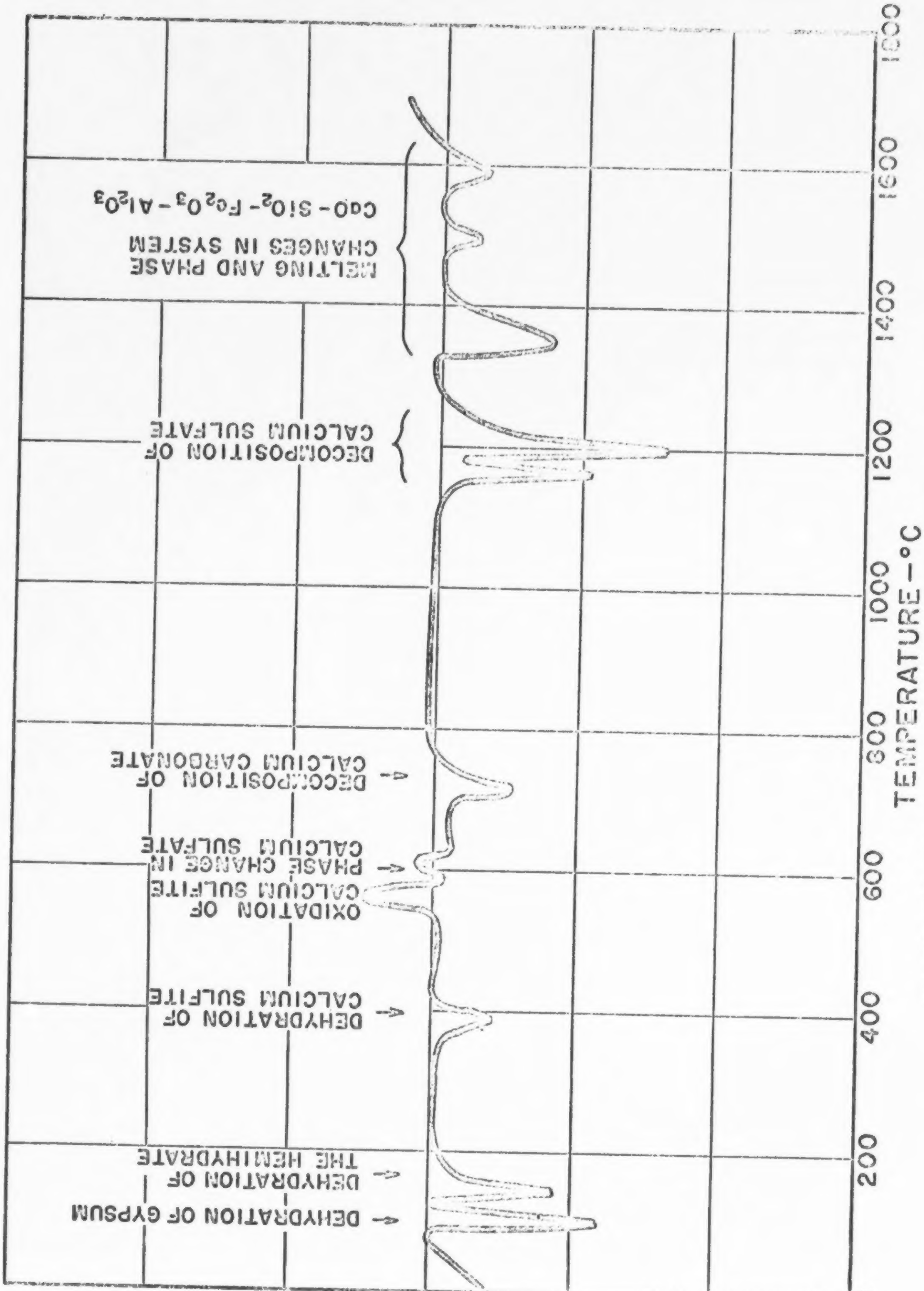


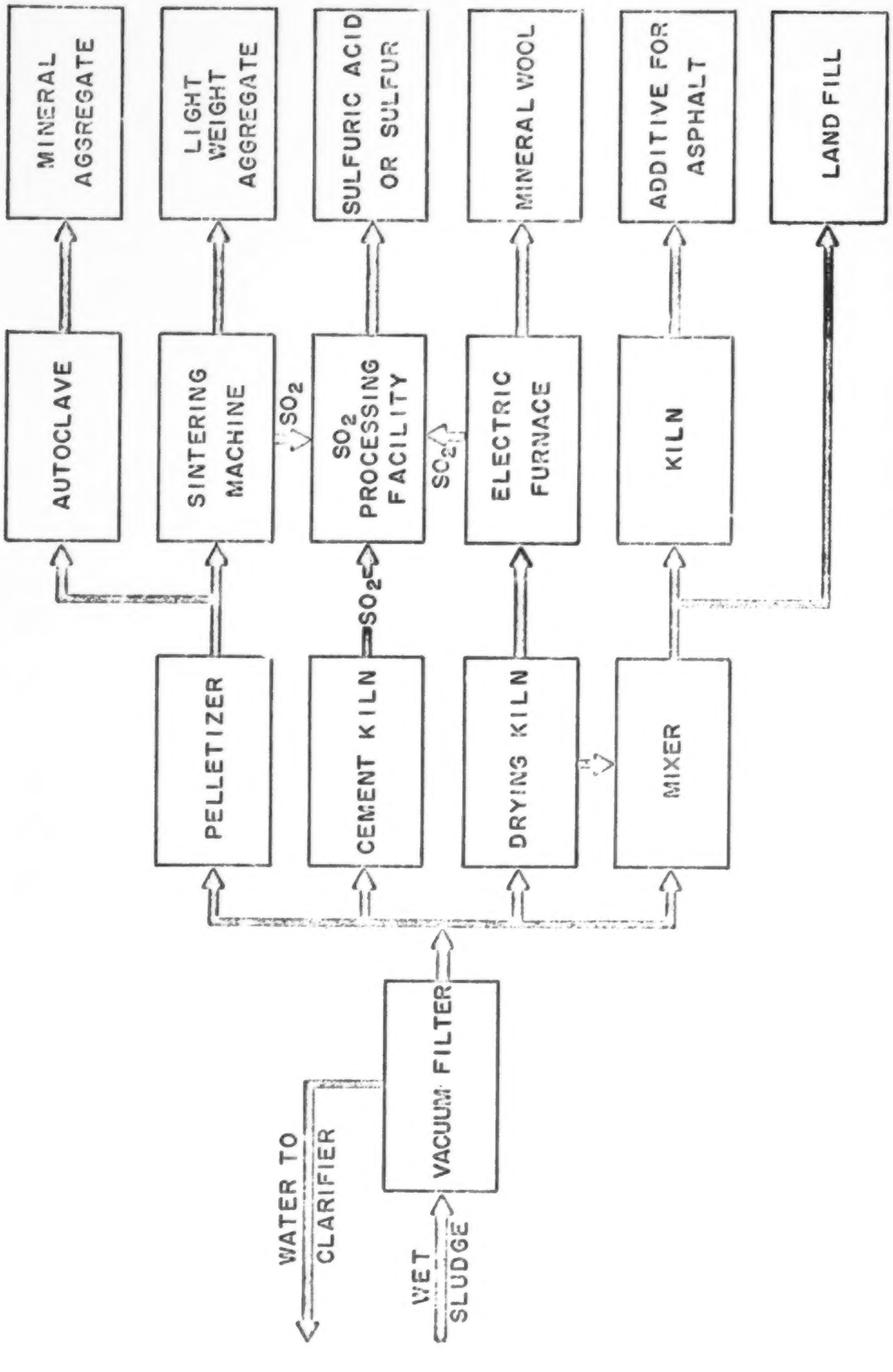
FIGURE -7

FIGURE -8



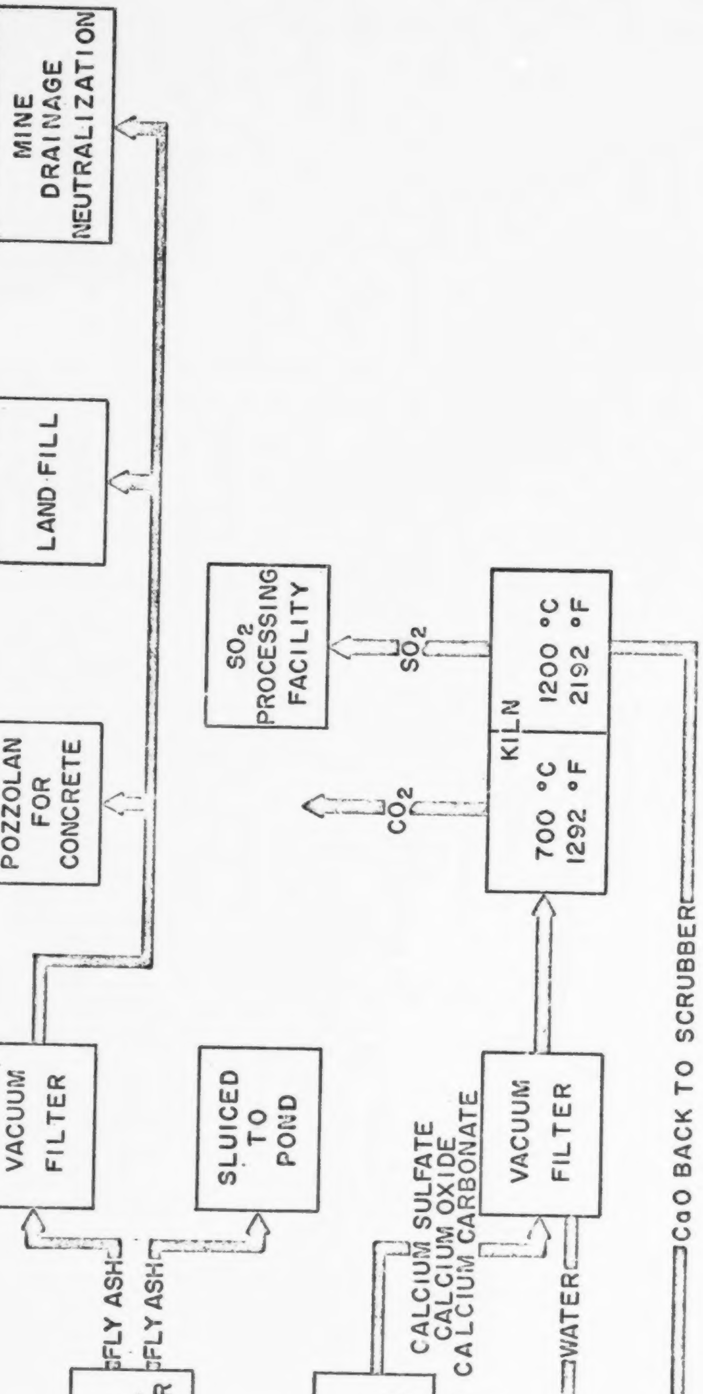
DIFFERENTIAL THERMOGRAM OF A FURNACE INJECTED MODE SLUDGE SAMPLE

FIGURE 9



SLUDGE DISPOSAL SCHEMES FOR A SINGLE SCRUBBER SYSTEM

FIGURE 10



SLUDGE DISPOSAL SCHEMES FOR A DUAL SCRUBBER SYSTEM

FIGURE 11

LIME SCRUBBING

of

SIMULATED ROASTER OFF-GASES

by

D. E. REEDY

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For

Presentation at the Second International
Lime/Limestone Wet Scrubbing Symposium

New Orleans, Louisiana

November 8-12, 1971

Introduction

In recent years, the lime/limestone absorption system has gained considerable impetus as an economically attractive flue gas SO_2 control scheme, over such alternates as lower sulfur fuels. There are other possible uses for the technology being developed for power plant flue gases, such as metallurgical roasting operations, but the level of understanding of the lime/limestone/SO_2 chemistry does not lend itself to reliable extrapolation to the higher SO_2 levels and SO_2/CO_2 ratios often encountered in industrial emission sources.

In this study, the absorption of SO_2 from an ambient air stream containing 1% SO_2 and 1% CO_2 utilizing a lime slurry was accomplished using a pilot plant Turbulent Contact Absorber (TCA)®. The main objective was to demonstrate the capability of high SO_2 removal efficiencies and to determine the chemical efficiency for lime usage under a specific set of conditions.

Description of Equipment

A schematic diagram of the pilot plant equipment set-up is shown in Figure 1.

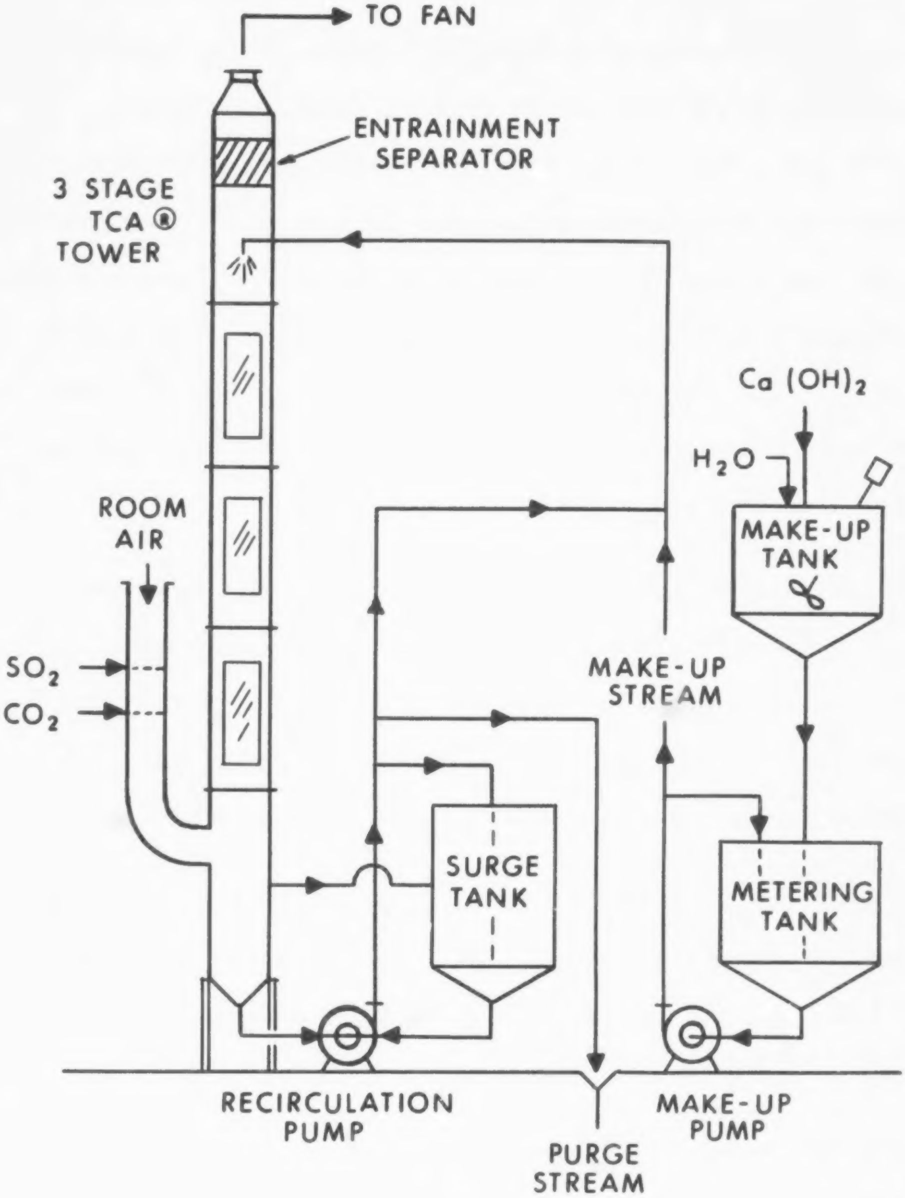

FIGURE 1 – EQUIPMENT FLOWSHEET

Vaporized SO_2 and CO_2 were injected into the ambient air inlet duct approximately four duct diameters ahead of the absorber. The absorber itself was one of our standard, one square foot Turbulent Contact Absorbers®. Three contacting stages, each containing approximately one cubic foot of static packing, were utilized in this study. Recirculation liquor was introduced countercurrent to the gas flow, above the top contacting stage, through a full cone nozzle. Figure 2 depicts the unrestrained contacting motion achieved with the spherical packing in a TCA®. The entrainment separator used in this study is similar to that shown in the illustration.

Liquor draining from the lower stage was collected in the scrubber sump connected in parallel with an agitated retention tank that provided 2-3 minutes holdup. The slurry purge from the system was withdrawn from the discharge of the recirculation pump.

Slurried, hydrated lime, with a particle size distribution similar to that shown in Figure 3, was added to the liquor recirculation line downstream of the purge withdrawal point.

Liquor samples referred to in subsequent sections were taken directly from the retention tank, while gas samples were withdrawn immediately after the entrainment separator.

Air Correction Division
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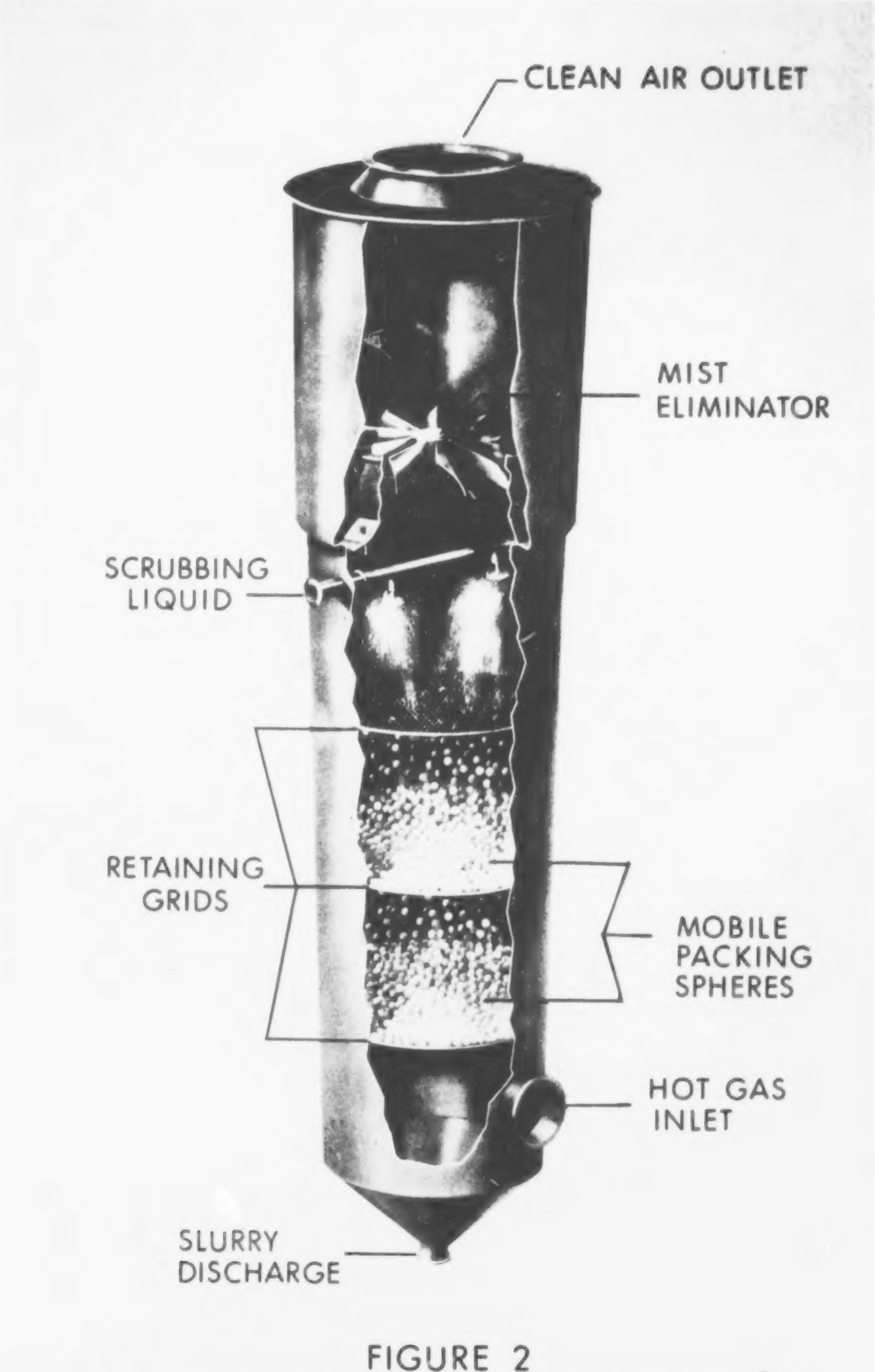
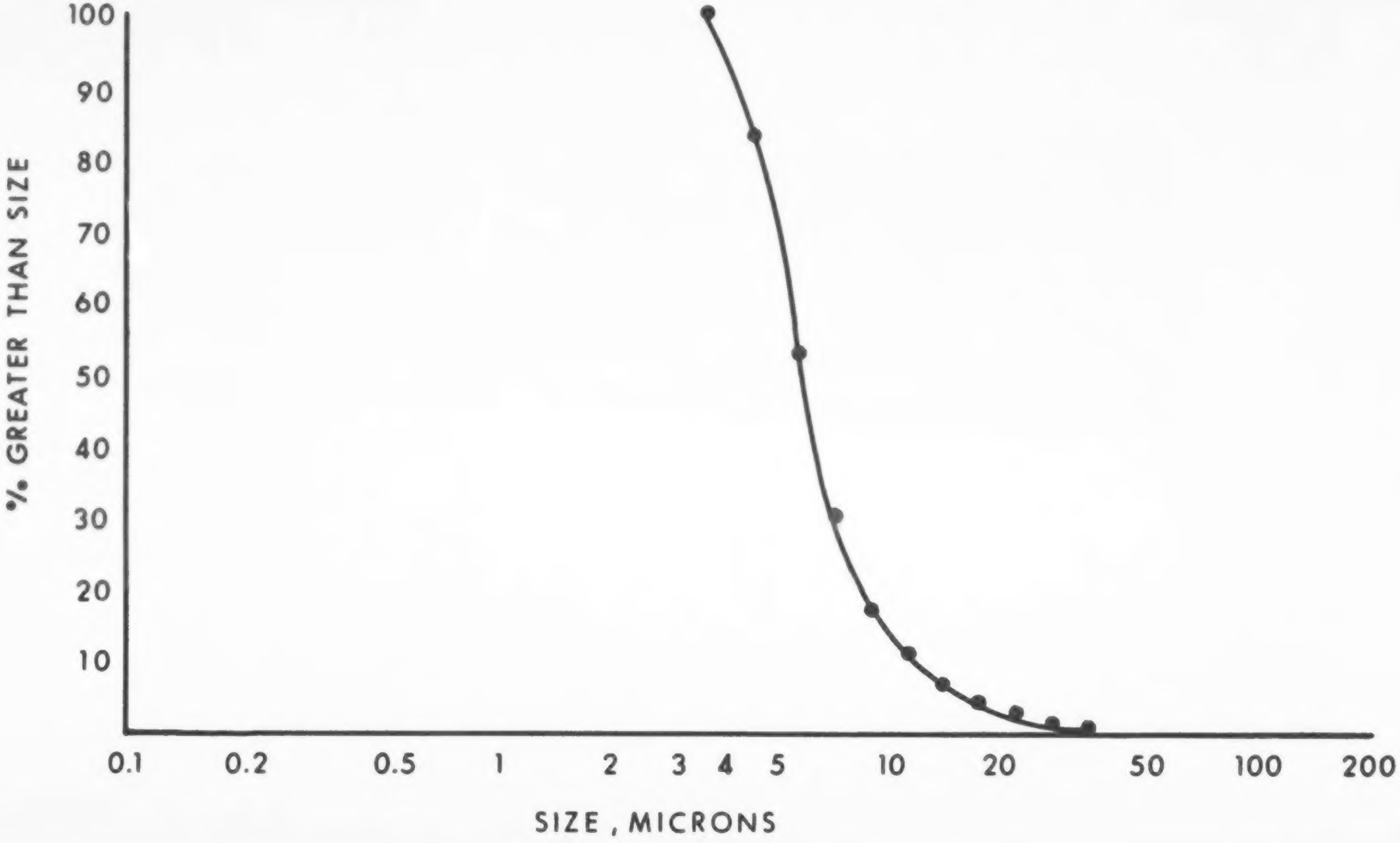


FIGURE 2
TURBULENT CONTACT ABSORBER ®

FIGURE 3
LIME PARTICLE SIZE DISTRIBUTION



Discussion of Results

Table I is a summary of the operating data from pilot plant operations. A quick analysis of these data yields some interesting observations.

Gas velocity variations, illustrated by a comparasion of Test 2 and Test 5, seemed to have a relatively small effect on SO_2 removal (the magnitude and direction of change in SO_2 removal in these two tests must be attributed to "data scatter"). Although the liquor residence time has been shown to be essentially a function of recirculation rate only, in a TCA® a comparison of results from Tests 1 and 4 would indicate that holdup time, or L/G, are not significant factors in SO_2 removal.

The controlling variable in this study is the pH of the scrubber outlet liquor. The relationship is shown in Figure 4. This is nothing new, of course, for many studies of limestone scrubbing of power plant flue gases have shown the importance of limestone "quality" when translated into terms of scrubber effluent pH.

TABLE I

SUMMARY OF PILOT PLANT DATA

Test Number	Gas Velocity, Ft./Min.	L/G, Gal/1000 CFM	Scrubber ΔP, in W.G.	Outlet Liquor		Inlet SO_2, Vol %	SO_2 Removal, %
				pH	% Solids		
1	900	58	9.5	8.0	-	0.92	82
2	630	82	7.5	5.8	-	1.32	65
3	800	69	8.5	13.0	17.8	1.01	98
4	800	82	8.5	8.0	-	1.01	78
5	800	85	9.2	5.8	17.8	1.01	73
6	820	73	8.9	11.2	-	1.04	89
7	820	73	8.9	12.7	7.0	1.04	98

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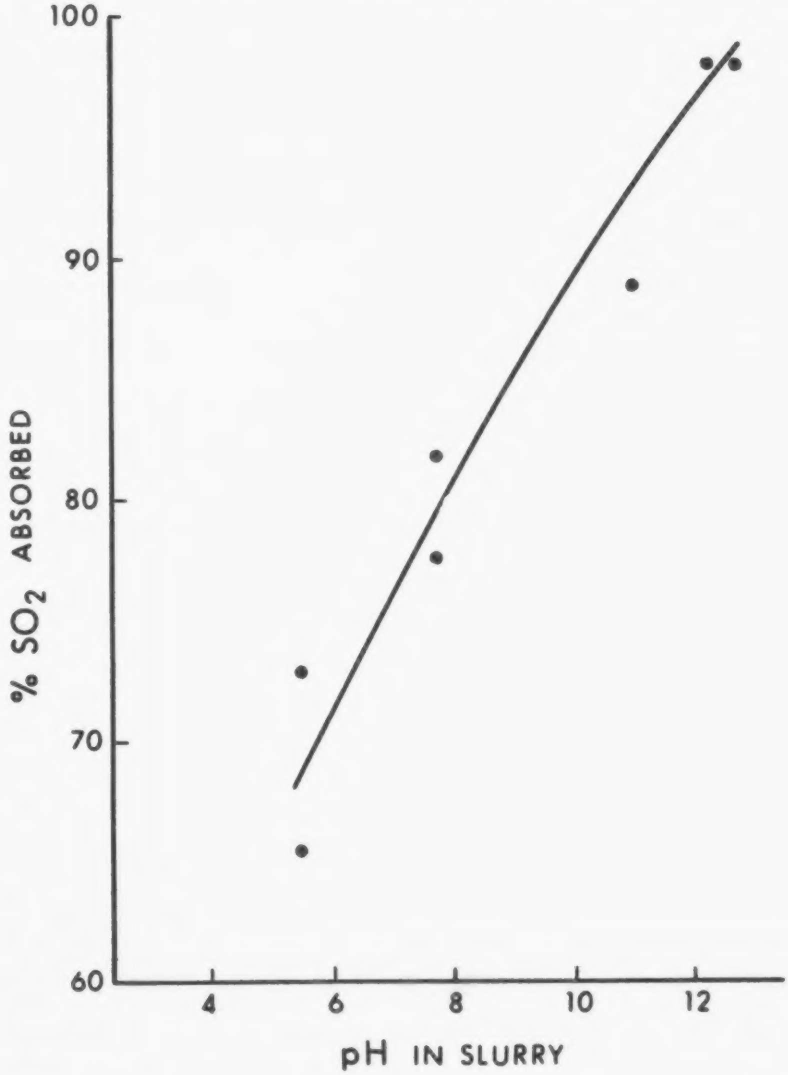
FIGURE 4
SO$_2$ ABSORPTION VS. pH



Slurry samples from several tests were analyzed for calcium, carbonate, sulfur and sulfite as shown in Table II, and then the solids were filtered from the slurry and analyzed for the same components. Assuming that the only sulfur species present are the sulfite and sulfate these data show that only a few percent of the hydrated lime input is being lost with the slurry purge stream. A somewhat higher percentage of the hydrated lime may be lost as carbonate, as shown by the following mol ratios:

Molar Ratios

Test	$CO_3^=/Ca^{++}$	S/Ca^{++}	$CO_3^=/S$	$SO_3^=/S$
3	0.16	0.76	0.22	0.96
5	0.09	0.97	0.09	0.93
7	0.11	0.90	0.12	0.91

These ratios would indicate that 10 to 15 percent of the calcium values are being lost as carbonate, but it should be pointed out that spot checks of various batches of the hydrated lime indicated that there was some carbonate present prior to its use in the absorption tower, probably as a result of exposure to the atmosphere.

TABLE II

RETENTION TANK ANALYSES

Test No.	3	5	7
Total Stream, Wt.%			
Calcium	5.5	5.3	2.2
Carbonate	1.1	0.7	0.2
Sulfur	3.3	4.2	1.7
Sulfite	4.2	-	2.4
Solids, Wt.%			
Calcium	34.1	29.8	28.7
Carbonate	8.3	3.7	4.7
Sulfur	20.6	23.1	20.7
Sulfite	49.8	54.0	47.3

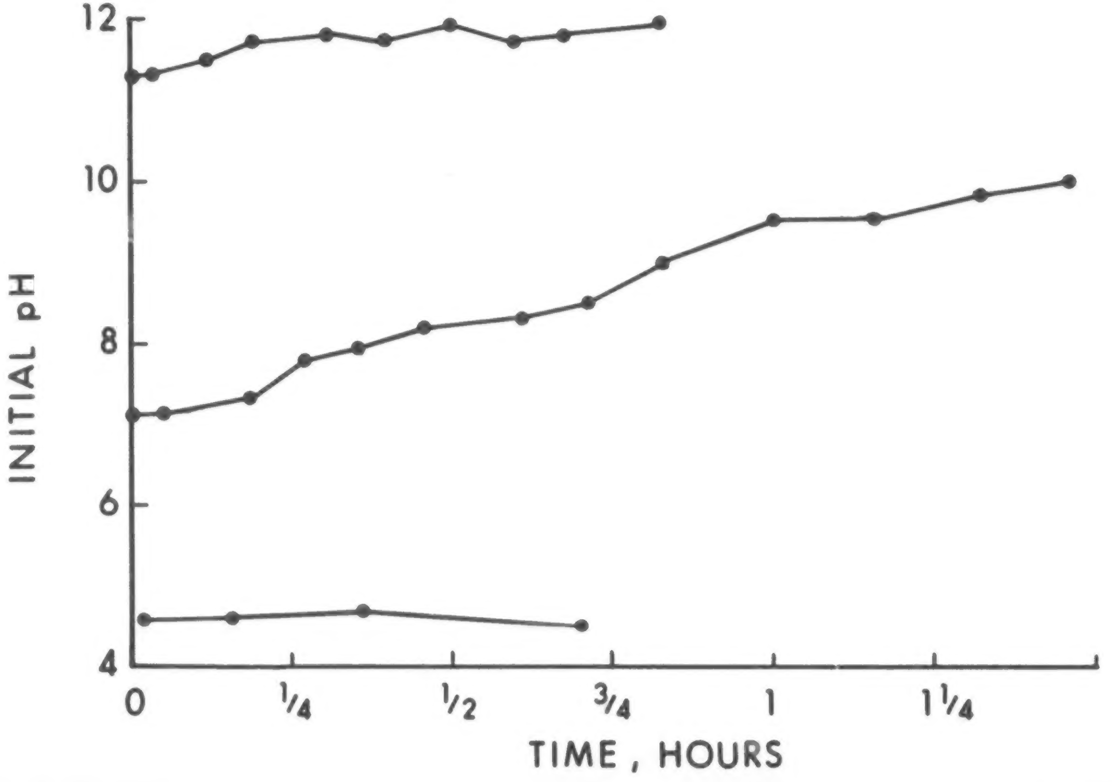
The data are consistent in that operation at a lower pH, Test 5, resulted in an increased rejection of CO_2 and higher utilization of calcium.

In Test 3, the makeup lime slurry concentration was about 10% while in Test 7 the makeup rate was approximately doubled and the input lime concentration cut in half. A comparison of the above mol ratios for these two tests would indicate that either the makeup slurry concentration or the recycle slurry concentration is affecting the loss of calcium values as carbonates.

The sulfite/sulfur ratio would indicate that very little sulfate is being formed in this operation, and that sulfate formation is relatively insentitive to pH. These test runs were of relatively short duration, however, and these numbers may not represent fully equilibrated operation.

Figure 5 shows that, at pH's above the neutral point, the liquid in the retention tank was not completely in equilibrium with the solids and that a long time was required for this equilibrium to be attained as the residual lime went into solution. Again, however, the amount of undissolved lime remaining in the slurry was very small.

FIGURE 5
SLURRY pH VS. TIME



Conclusions

I. Lime scrubbing can achieve high SO_2 removal efficiencies from gases containing moderately high SO_2 levels.

II. Recirculation liquor pH is a dominant factor in this operation and must be maintained at a high level to achieve high scrubbing efficiencies.

III. In spite of the high pH required to achieve the desired SO_2 removal, chemical efficiencies for lime utilization in excess of 80% can be realized.

##########

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2. Pollock, W.A., Tomany, J.P. and Frieling, G., ASME 66-WA/CD-4 (1966).

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